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IN ENGLISH TRANSLATION

INVESTIGATION OF BASIC FERRIC SALTS

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The question of basic salts of ferric oxide is far from having been clarified up to the present time. The kinetics of hydrolysis for ferric salts, and the formation conditions of basic salts have not been adequately studied. Certain of the more important properties of soluble basic salts of ferric oxide, and their behavior, have been studied mainly by Soviet investigators [1-3]. A study of basic salt precipitates resulting from the sulfate of ferric oxide with various alkalies has led to a considerable number of compounds with varied ratio between ferric oxide and sulfur trioxide [4-5]. There exists no unanimous point of view concerning the nature of such products obtained when alkali is reacted with ferric salts, and it is not possible to draw any definite conclusions to the composition and number of basic salts of ferric oxide.

To investigate the interaction of ferric oxide salts with alkali, the author used a physico -chemical method of analysis which was developed by Kurnakov and his school.

EXPERIMENTAL

Study of the sulfates of ferric oxide basic salts was carried out by the isothermal method. To carry out each experiment at 25°, the appropriate volumes of $Fe_2(SO_4)_3$ and KOH were taken.

0.0409 m.-eq. of H_2SO_4 was taken per 1 m.-eq. of $Fe_2(SO_4)_3$ in the initial solution of ferric salt. The pH of the solution was equal to 1.4. Standard flasks were used for work on solubility determinations, equipped with stirrer and oil seal to prevent absorption of carbon dioxide from the air. The flasks were placed in a water thermostat at 25°. Temperature variation did not exceed $\pm 0.1°$. Accurately measured volumes of $Fe_2(SO_4)_3$ were poured into the flasks, stirring begun, and finally the corresponding volumes of potassium hydroxide solution added drop by drop from a burette. Continuous 24-hour stirring was carried out, to the establishment of chemical equilibrium between the liquid and solid phases, determination of which equilibrium was carried out by coincidence of analytical results for ferric ions, or sulfate radical, in the last samples of transparent supernatant over the precipitate. After attainment of equilibrium, stirring was terminated and chemical analysis carried out according to the Schreinemaker residue method. The amounts of ferric oxide, potassium, and sulfate ions, were determined. Trivalent iron was determined iodometrically, sulfate ion gravimetrically, according to the method developed by Nikitina and Babaeva [6], quantitative determination of potassium ions being carried out as sulfate by the gravimetric procedure. The pH of the solutions was determined by glass electrode. For determination of the composition of solid phases, portions of the complex quaternary system $K_2O-Fe_2O_3-SO_3-H_2O$ were investigated. Experiments carried out belong to the projection ray study of characteristic points for composition of the system on the plane for $KOH-Fe(OH)_3-H_2SO_4$.

The portion of indicated quaternary systems studied can be graphically represented by a tetrahedron, at one of whose corners is the constituent water, and at the base of which tetrahedron three of the components in hydrated form: KOH, H_2SO_4, $Fe(OH)_3$.

There is given in Fig. 1 the construction of such a tetrahedral space diagram in the form of an equilateral triangle. From the appearance of the diagram constructed the chemical nature of the substances formed in the system can be evaluated. In Fig. 1 the apices of the triangle correspond to pure components, and the sides to the systems having two components. The compositions of the initial mixtures for liquid and solid phases for the established equilibrium (Fig. 1) are expressed in milliequivalent percentages for the amounts of iron, potassium and sulfate ion.

From the diagram (Fig. 1) the following deductions can be made.

1. In that section of the diagram which is rich in iron ions (experiments 1-7) where for the weight quantity of potassium hydroxide taken, there was used 86.7 - 62.5 m-eq. % of $Fe_2(SO_4)_3$, the lines converge at one spot on the diagram. It is known that if points are present on the lines which determine the composition of the solid phase, and
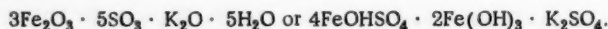
TABLE 1

Compositions of the initial compounds taken for experiment

Experiment No.	Percent milliequivalent		Milliequivalents available for 40 ml of initial mixture.			
	Iron•	KOH••	K^+	Fe^{+++}	SO_4^{--}	OH^-
1	90.9	9.1	3.446	34.50	35.91	2.036
2	86.7	13.3	6.260	40.73	42.39	4.60
3	82.1	17.9	6.67	30.67	31.92	5.42
4	77.5	22.5	10.43	35.94	37.41	8.96
5	72.1	27.9	10.38	26.83	27.93	9.28
6	68.1	31.9	11.68	24.92	25.94	10.66
7	62.5	37.5	13.78	23.00	23.94	12.84
8	58.4	41.6	15.01	21.08	21.95	14.14
9	52.6	47.4	17.29	19.17	19.95	16.51
10	43.4	56.6	20.02	15.33	15.96	19.39
11	32.2	67.8	24.21	11.50	11.97	23.74
12	22.3	77.7	26.69	7.67	7.98	26.38
13	11.3	88.7	30.02	3.833	3.990	29.86

if these lines within the diagram intersect, then their point of intersection characterizes the solid phase as a chemical compound of definite composition. For 1 mole of $Fe_2(SO_4)_3$, there is assigned for this intersection point on the diagram 2.5 moles of $Fe(OH)_3$ and 0.75 mole of K_2SO_4. Hence the solid phase found should represent a basic salt of ferric oxide of the composition:

$$4Fe_2(SO_4)_3 \cdot 10Fe(OH)_3 \cdot 3K_2SO_4.$$

The simplest formula for this salt is

$$3Fe_2O_3 \cdot 5SO_3 \cdot K_2O \cdot 5H_2O \text{ or } 4FeOHSO_4 \cdot 2Fe(OH)_3 \cdot K_2SO_4.$$

There is given in Table 2 the composition of precipitates, calculated according to the data from chemical analysis.

For the indicated experiments (1-7), at pH 1.8, there was formed a fine cyrstalline anisotropic, light-yellow precipitate. Chemical analysis of these cyrstalline precipitates confirmed the chemical composition of the solid phase found by the graphical method according to the diagram. In experiment 7, a crystalline precipitate was formed with utilization of the entire amount of iron contained in the original mixture. In experiment 1 with a ferric ion content of 90.9 m-eq. %, traces of crystalline precipitate were obtained, despite continuous around-the-clock stirring for 350 hours.

TABLE 2

Chemical analysis of the precipitate

Experiment No.	No. of Fe^{+++} ions in the initial mixture (in m-eq. %)	No. of milliequivalents contained in 1 g. of precipitate			Chemical composition of the solid phase.
		K^+	Fe^{+++}	SO_4^{--}	
2	86.7	1.320	12.84	6.980	$Fe_2(SO_4)_3 \cdot 2.5Fe(OH)_3 \cdot 0.7K_2SO_4$
3	82.1	1.622	14.984	8.107	$Fe_2(SO_4)_3 \cdot 2.6Fe(OH)_3 \cdot 0.75K_2SO_4$
4	77.5	1.560	15.19	8.260	$Fe_2(SO_4)_3 \cdot 2.5Fe(OH)_3 \cdot 0.7K_2SO_4$
5	72.1	1.650	13.14	7.600	$Fe_2(SO_4)_3 \cdot 2.4Fe(OH)_3 \cdot 0.8K_2SO_4$
6	68.1	1.200	9.830	5.600	$Fe_2(SO_4)_3 \cdot 2.5Fe(OH)_3 \cdot 0.8K_2SO_4$
7	62.5	1.048	9.750	5.250	$Fe_2(SO_4)_3 \cdot 2.6Fe(OH)_3 \cdot 0.75K_2SO_4$

The line in this experiment passes through a point which determines the composition of the solid phase in experiment 2.

• 0.9583 N $Fe_2(SO_4)_3$.
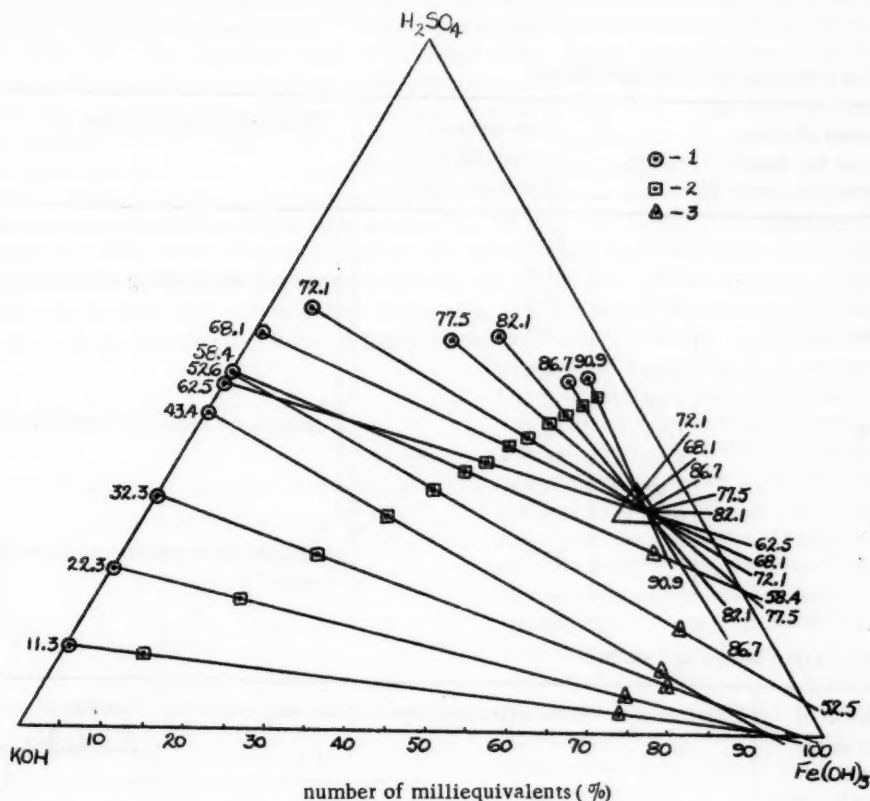
•• 0.8340 or 0.8614 N KOH.

Fig. 1. Structure of the tetrahedron diagram for the system $K_2O-Fe_2O_3-SO_3-H_2O$.
1) Co mposition of the liquid phase, 2) composition of the initial mixture, 3) composition of the solid phase.

2. The directions of the lines in that section of the diagram with a content of 58.4 - 52.6 m-eq.% of ferric ions attest to the fact that at pH 2.5 - 2.67 a mixture of crystalline salt and ferric oxide hydrate results (compositions of the liquid phases in these experiments approximating the composition of pure potassium sulfate solutions.).

3. The lines in the section containing 43.4 - 11.3 m-eq. % of ferric ions (experiments 10-13) converge at a point which is close to the point for pure ferric oxide hydrate. The amorphous precipitates, red-brown in color, obtained in experiments at pH 11.0 - 13.45, should thus represent adsorption products of alkali and potassium sulfate with the hydrate of ferric oxide.

4. It can be seen from the diagram that the smallest value for ratio of segment length on the line from the point for total composition of initial mixture to the point of composition for residue (a_2), and from the point of composition for initial mixture to the points of composition of liquid phase (a_1), corresponds to experiments 5 and 6 (0.49); thus, to obtain the highest yield of basic crystalline salts, there should be taken such amounts of $Fe_2(SO_4)_3$ and KOH that there is available 28-32 m-eq. of alkali in the initial mixture for each 72-68 m-eq. of iron salt.

In determining specific relationships for the ratio a_2/a_1, time is taken to establish chemical equilibrium between liquid and solid phases.

It can be seen from Table 3 that for the section of resulting cyrstalline and amorphous precipitates, chemical equilibrium very slowly becomes established in those experiments, where the smallest amounts of precipitates resulted (31-34 days); especially slowly established was the equilibrium in experiment 8, in which a mixture

of crystalline and amorphous precipitates was forming (86 days). A series of investigations was carried out with the crystalline precipitates. They were boiled in the mother liquor and with water in an apparatus equipped with reflux condenser. Following each operation (Table 4), potassium ions were found in the wash waters only for experiment 8.

TABLE 3
Time required to establish chemical equilibrium

Experiment No.	Content of ferric ions in the initial mixture(in m-eq.%)	$a_2 : a_1$	Time required to establish equilibrium (in days)	Character of precipitates
13	11.3	6.29	31.0	
12	22.3	2.98	31.0	Section for resulting amorphous precipitates
11	32.2	2.16	5.1	
10	43.4	1.50	5.0	
2	86.7	4.29	34.0	
3	82.1	1.18	32.5	
4	77.5	1.02	31.0	Section for resulting cyrstalline precipitates
5	72.1	0.49	14.6	
6	68.1	0.49	4.8	
7	62.5	0.60	5.3	
8	58.4	0.80	86.0	Mixture of crystalline and amorphous precipitates

TABLE 4
Crystalline precipitates, boiled and washed

Experiment No.	Content of ions in the initial mixture(in m-eq.%)	Treatments to which crystalline precipitates were subjected	Number of moles per 1 mole of $Fe_2(SO_4)_3$	
			$Fe(OH)_3$	K_2SO_4
4	77.5	Precipitate not washed with water	2.5	0.7
4	77.5	Precipitate washed with water to disappearance of reaction for SO_4^{--} ion	2.5	0.8
4	77.5	Precipitate washed twice with water in apparatus equipped with reflux, for 18 and 10 hours, and washed with water to disappearance of SO_4^{--} test.	3	0.8
5	72.1	Precipitate not washed with water	2.42	0.8
5	72.1	Precipitate boiled 2 hours in mother liquor, then 1 hour with water, and washed with water to disappearance of SO_4^{--} reaction	2.94	0.82
6	68.1	Precipitate not washed with water	2.5	0.8
6	68.1	Precipitate washed with water to disappearance of SO_4^{--} reaction	2.5	0.8
6	68.1	Precipitate was boiled for 2 hours in mother liquor, and then for 1 hour with water, washed with water to disappearance of SO_4^{--} reaction	2.95	0.8
8	58.4	Precipitate not washed with water	5.15	1.36
8	58.4	Precipitate boiled for 18 hours in mother liquor and then twice with water for 3 and 6 hours, and washed with water to disappearance of reaction for SO_4^{--} and K^+	7.3	0.9

The following deductions can be made from Table 4:

1) chemical composition of crystalline precipitate washed with water remains unchanged, 2) crystalline precipitate

begins to hydrolyze upon boiling with water, the potassium sulfate not washing out, 3) in experiment 8, the precipitate representing a mechanical mixture of crystalline basic salt and iron hydroxide, hydrolyzes to a considerable extent, and in this case, washing out of potassium sulfate is observed. In all probability, in forming this reaction, potassium sulfate is adsorbed by ferric hydroxide. X-ray photographs of the crystalline precipitate and of the crystalline ferric hydroxide have demonstrated that the form of the crystalline precipitate of ferric oxide sulfate basic salt is not conditioned by the crystalline form of the ferric hydroxide. The crystalline basic salt of ferric sulfate and the crystal hydrate of ferric sulfate, the amorphous hydrate of ferric oxide, and a mixture of the crystalline basic salt and ferric hydroxide, have been investigated thermographically.* Heating curves for these substances are given in Figs. 2-5. Time is plotted along the horizontal axis on the thermograms, and temperature on the vertical axis. The zero line is marked by a broken line. Observations were carried out for 3 hours. An automatic registering Kurnakov apparatus was used for recording of temperature and time. Analysis of the differential heating curve for crystalline basic ferric sulfate salt (Fig. 2) indicates that the first two endothermic effects correspond to a water loss (90 and 170°), where it can apparently be assumed that at 90° the water of crystallization is removed, and at 170°, in all probability, more rapid removal begins of the water which is more closely bound to the basic salt. A third endothermic effect (365° and 410°) possibly characterizes a partial decomposition of the basic salt, with formation of $Fe_2(SO_4)_3$, and it should be assumed in this case that at 410° water formation proceeds at the expense of hydroxyl groups of the basic salt. The fourth exothermal effect (510°) corres-

Fig. 2. Curve for the crystalline basic ferric sulfate salt on heating.

ponds, in all probability, to the existence of a regrouping of the atoms inside of the given substance, and to the formation of more stable compounds. The last two thermal effects (710°-775°) are characterized by more profound decomposition of the salt; here is possibly decomposition of $Fe_2(SO_4)_3$ into ferric oxide and SO_3. We might mention that the decomposition of $FeSO_4$ into ferrous oxide and SO_3 proceeds at 725° [7]. Without dwelling upon analysis of other thermograms, a comparison of the heating curves for three substances (Figs. 2,3 and 4) allows the following deductions: there are no $Fe_2(SO_4)_3$ and $Fe(OH)_3$ as individual chemical compounds in the crystalline precipitate. The general outline of the heating curve in Fig. 5 indicates that the precipitate obtained in Experiment 8 is not an individual substance (diffuseness of the planes, insufficiently definite thermal breaks). Upon drying 5.0098 g of the crystalline basic salt for 126 hours at 100°, 0.476 g of water was lost; it failed to reach constant weight. For this amount of water, recalculating for 1 mole of $4FeOHSO_4 \cdot 2Fe(OH)_3 \cdot K_2SO_4$ gives 5.594 moles of water (Fig. 6).

If we assume that the process did not go to completion, then a hypothesis can be made that 6 molecules of crystallization water enter into the composition of 1 molecule of the indicated salt. Thus, this latter experiment, and the heating curves indicated, suggest that the crystalline basic salt is a crystalline hydrate, and hydroxyl groups should enter into the composition of this salt. It should be mentioned that upon investigating a portion of the complex quaternary system $K_2O-Fe_2O_3-SO_3-H_2O$, the hydrated oxides were unaffected. The diagram (Fig. 1) gives a picture of the quantitative relationships of all components except water. The amount of water in the system was not determined every time. Crystalline precipitates of the basic ferric salt are insoluble in water and poorly soluble in hydrochloric acid. 21 ml. of 1.479 N HCl is needed to dissolve 0.0705 g of crystalline basic salt precipitate at room temperature.

In another experiment, complete dissolution of the precipitate was observed only at 100° after addition of 10 ml of 1.479 N HCl to 0.1051 g of the crystalline basic salt. In Fig. 7 a potentiometric curve for titration of 0.1160 g of this salt at 74° is shown. Results of the potentiometric titration indicated that interaction of hydrochloric acid with the basic groups of the salt proceeds with extreme slowness. Such phenomenon, in all probability, is explainable by the fact that the ferric ions in the basic salt are bound quite securely with the hydroxyl ions of oxygen. If there be taken into account the investigations of structure for the polymeric monohydrate $(FeOOH)_4$ [8,10], the polynucleic chain of complexes for basic salts of chromium, and the results of the author's investigations, it can then be considered that the polynucleic stable complex ion enters into the composition of the basic crystalline salt. Thus, the salt can have the structure $K_2^+[Fe_6^{+++}(OH)_{10}^-(SO_4)_5^-]^{--}$. If the coordination number for iron is assumed to be 6, and that
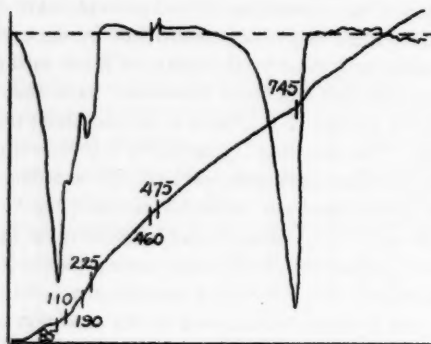
Fig. 3. Heating curve for the crystal hydrate of ferric sulfate.
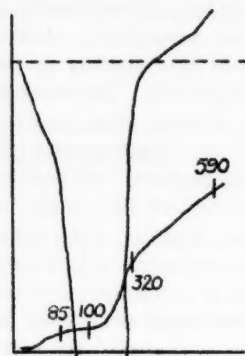
Fig. 4. Heating curve for amorphous ferric hydroxide.
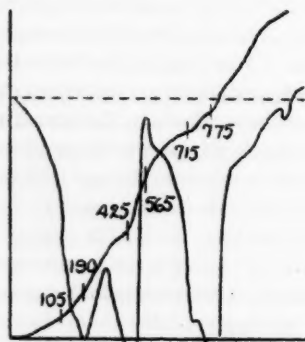
Fig. 5. Heating curve for the mixture of crystalline basic salt and ferric hydroxide.

the OH^- and SO_4^{--} groups are maximally utilized for occupation of spaces in the coordination spheres of the iron atoms, then the crystallohydrate structure for the complex salt can be presented as follows:

Fig. 6. Water loss upon drying the basic crystalline ferric sulfate salt.

The additional 6 water molecules, not accounted for in the simplest formula, are underlined. A hypothesis can be made that these water molecules were indeed split off upon drying the basic salt at 100° (Fig. 6); however, water evolves from the hydroxyl groups at higher temperatures (as reflected in the thermograms). If there be taken into consideration the fact that the drying process for the precipitate at 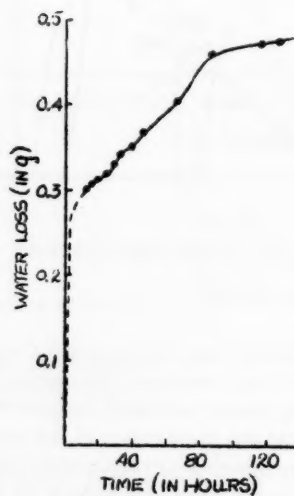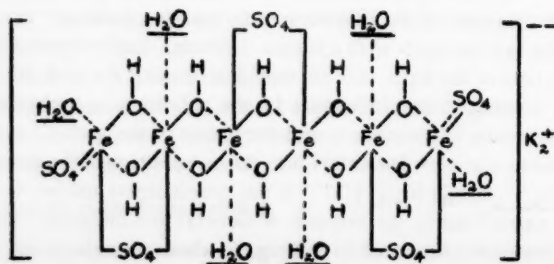100° is not complete, then the 5.6 molecules of water found in this experiment, which are split off at 100°, gives good agreement with the theoretical calculation. Proceeding from the quoted structure for the complex basic double crystalline salt of ferric sulfate,
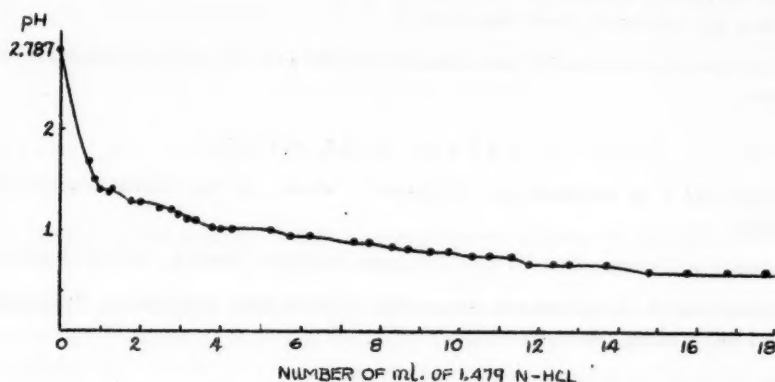

Fig. 7. Potentiometric titration of the crystalline basic salt of ferric sulfate
1. Number of ml. of 1.479 N-HCl

the difficult solubility of this salt in mineral acid can be explained, justifying results of the potentiometric titration. The interaction of hydronium ions with hydroxyl ions, which enter into the composition of the polynuclear complex ferric ion, proceeds with extreme slowness. It is known from the literature [11,12] that the crystalline salt of aluminumsulfate $(Al_2O_3H)_2^+ SO_4^{--}$ reacts in an analogously slow manner.

Fine crystalline precipitates were also obtained by interaction of ferric sulfate with calcium carbonate. Data on the interaction of $Fe_2(SO_4)_3$ with NaOH are given in Table 5. For the initial mixtures of 62.5 and 72.1 m-eq.% of ferric sulfate, 37.5 and 27.9 m-eq. % of sodium hydroxide were taken. Round-the-clock stirring was carried on for 25 days. After termination of the experiment, the resulting amorphous brown-colored precipitates were filtered off and washed with water to the disappearance of reactions for the ions of sulfate and potassium in the wash water.

TABLE 5
Interaction of $Fe_2(SO_4)_3$ with NaOH

Experi-ment No.	Composition of initial mixture (in		Batch of pre-cipitate taken for analysis (in g)	No. of milliequivalents in 1 g of precipitate		No. of moles of $Fe(OH)_3$ available per 1 mole of $Fe_2(SO_4)_3$ in the precipitate	No. of milliequi-valents of sodium ions in the preci-pitate
	$Fe_2(SO_4)_3$	NaOH		$Fe_2(SO_4)_3$	$Fe(OH)_3$		
1	160	95.80	1.5271	0.907	4.769	10.60	None
2	160	61.94	1.4527	0.976	5.264	10.79	None

It can be seen in Table 5 that the sodium ions do not enter into the composition of the obtained amorphous precipitates, in contrast to similar experiments on the interaction of $Fe_2(SO_4)_3$ with potassium hydroxide. Thus, variable behavior of the $Fe_2(SO_4)_3$ solutions when acted upon by alkali (NaOH, KOH) is conditioned by selection of the alkaline cation. used. Formation of crystallization precipitates was not observed upon interaction of ferric chloride with potassium hydroxide, sodium hydroxide or calcium carbonate.

SUMMARY

As a result of the investigations conducted on basic salts of ferric sulfate, variable behavior of $Fe_2(SO_4)_3$ solutions when acted upon by sodium hydroxide potassium hydroxide has been demonstrated.

1. Precipitates resulting by interaction with sodium hydroxide are amorphous and do not contain sodium sulfate.

2. Precipitates obtained by interaction of $Fe_2(SO_4)_3$ with potassium hydroxide are finely crystalline and contain potassium sulfate in chemically-bound state. They are in the form of a basic salt, possessing the simple formula $4FeOHSO_4 \cdot 2Fe(OH)_3 \cdot K_2SO_4$. It has been demonstrated that the salt in question is a crystalline hydrate and contains a stable, polynuclear complex ion, the structure of which can be represented as $K_2^+ \ [Fe_6^{3+}(OH)_{10}^-(SO_4)_5^- \ (H_2O)_6]^{--}$.

3. The range of concentration of initial substances wherein the precipitates formed are either the crystalline basic salt or are in the form of amorphous ferric hydroxide, with adsorbed alkali and adsorbed potassium sulfate, or are mixtures of these two substances, have been studied.

4. Upon interaction of ferric chloride with alkali hydroxide and with calcium carbonate, crystalline precipitates are not formed.

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COMPOSITION OF SLIGHTLY SOLUBLE COMPOUNDS PRECIPITATED BY BASES FROM NICKEL SALT SOLUTIONS IN THE PRESENCE OF BORIC ACID

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The addition of bases to salt solutions of many metals produces slightly soluble hydroxides or more complex compounds.

The composition of these slightly soluble compounds and the standard isobaric potentials at which they form may be computed by the measurement of pH (in equilibrium with the solid phase), as a function of the activity of metal salts in solution [1,2].

Complex slightly soluble compounds may be formed from a metal hydrate and the salt of the same metal ($x[Me_bA_d] \cdot y[Me(OH)_n]$), or may contain molecules of foreign compounds (if the latter are present in the solution.).

Obviously, only the first type of slightly soluble compounds may be formed in pure sulfate solutions: their compositions and standard isobaric potentials have been computed in accordance with the general formula:

$$pH = \frac{\Delta Z^0_{(basic}}{2.3nyRT} - \frac{y + bx + dx}{ny} \log a_\pm - \frac{1}{ny} \log \frac{b(y + bx)^d dx}{\left(b^{\frac{b}{b + d}} d^{\frac{d}{b + d}} \right)^{y + bx + dx}} - \log K_W, \qquad (1)$$

where ΔZ^0_{basic} is the standard isobaric potential at which the basic salt begins to form, $a_\pm$ is the activity of the metal salt in solution, and K_W is the ion product of the water.

Study of the formation of slightly soluble compounds consisting of metal hydrates and molecules of foreign substances in solutions is also of interest, however.

Rotinyan and Zeldes [3,4] directed attention, a few years ago, to the fact that the addition of boric acid to nickel salt solutions resulted, upon titration with alkali, in the reduction of pH at the beginning of the formation of the solid phase.

At that time no explanation was found for this phenomenon, but after Keshan and his associates [5] discovered the existence of an entire series of slightly soluble metal borates, it became possible to relate the reduction in pH at the beginning of the appearance of the solid phase to the formation of boron-nickel compounds of lower solubility than that of pure nickel hydroxide. Thereupon it was decided to subject the problem of boron-nickel compound formation to more detailed investigation.

The foregoing certainly contradicts the very widespread opinion which holds the role of boric acid in a nickel electrolyte to be limited merely to the buffering properties of boric acid as a weak electrolyte [6]. It was therefore necessary to begin by independently demonstrating this view to be incorrect. This was confirmed by the potentiometric titration curves of boric acid and nickel sulfate solutions and mixtures thereof. Experience has shown the buffer branches of potentiometric titration curves of pure boric acid and nickel sulfate solutions to appear at much higher pH than in solutions containing a mixture of nickel sulfate and boric acid.

This difference in the curves cannot be explained other than by the assumption that the composition of the solid phase is qualitatively different in the presence of boric acid than when it is absent from the solution.

If, in the general case, the composition of the solid phase be represented by the formula $xNiSO_4 \cdot yNi(OH)_2 \cdot zH_3BO_3$ and if it be considered that this compound is in equilibrium with the solution*, i.e.,

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* We are considering only the first stage dissociation of boric acid.

$$zH^+ + zH_2BO_3' + (x + y) Ni^{++} + 2yOH' + xSO_4'' \rightleftarrows xNiSO_4 \cdot yNi(OH)_2 \cdot zH_3BO_3, \tag{2}$$

the following may be written:

$$z\Delta Z_6^0 + RT\ln a_{H+}^z + z\Delta Z_7^0 + RT \ln a_{H_2BO_3'}^z + (x + y)\Delta Z_2^0 + RT \ln a_{Ni++}^{(x + y)} + 2y\Delta Z_3^0 + RT \ln a_{OH'}^{2y} + x\Delta Z_4^0 +$$

$$+ RT \ln a_{SO_4''}^x = \Delta Z_5^0. \tag{3}$$

In Equation (3) the activity of the solid phase is as usual taken as unity. ΔZ_2^0, ΔZ_3^0, ΔZ_4^0, ΔZ_6^0, ΔZ_7^0 and ΔZ_5^0 represent the standard isobaric potentials at which Ni^{++}, OH', SO_4'', H^+, H_2BO_3' and the slightly soluble compounds are formed.

As

$$K_{H_3BO_3} = \frac{a_{H^+} \, a_{H_2BO_3'}}{a_{H_3BO_3}} \tag{4}$$

and

$$a_{OH'} = \frac{K_W}{a_{H^+}}, \tag{5}$$

therefore

$$z\Delta Z_6^0 + z\Delta Z_7^0 + RT \ln K_{H_3BO_3}^z + RT \ln a_{H_3BO_3}^z + (x + y)\Delta Z_2^0 + RT \ln a_{Ni++}^{x + y} + 2y\Delta Z_3^0 + RT \ln K_W^{2y} - RT \ln a_{H^+}^{2y} + x\Delta Z_4^0 +$$

$$+ RT \ln a_{SO_4''}^x = \Delta Z_5^0 \tag{6}$$

or

$$pH = \frac{\Delta Z_5^0 - (x + y)\Delta Z_2^0 - 2y\Delta Z_3^0 - x\Delta Z_4^0 - z\Delta Z_6^0 - z\Delta Z_7^0}{2.3 \cdot 2yRT} - \frac{z}{2y}\log a_{H_3BO_3} - \frac{1}{2y}\log \, a_{Ni++}^{(x + y)} a_{SO_4''}^w - \log K_W - \frac{z}{2y}\log K_{H_3BO_3}. \tag{7}$$

As

$$\Delta Z_5^0 - (x + y)\Delta Z_2^0 - 2y\Delta Z_3^0 - x\Delta Z_4^0 - z\Delta Z_6^0 - z\Delta Z_7^0 = \Delta Z_{st}^0 \tag{8}$$

Z^0 is the standard isobaric potential of reaction (2), $a = m\gamma$, $m_{SO_4''} = m_{Ni++} = m_c$ (m=the molality of the salts and ions; γ = the coefficient of activity), equation (7) may be rewritten as follows:

$$pH = \frac{\Delta Z_{st}^0}{2.3 \cdot 2yRT} - \frac{z}{2y}\log a_{H_3BO_3} - \frac{2x + y}{2y}\log a_+ - \log K_W - \frac{z}{2y}\log K_{H_3BO_3}. \tag{9}$$

Equation (9) was derived for a particular case; however, it may be worked out without difficulty in a general form applicable to complex slightly soluble compounds, regardless of composition. It differs from formula (1) not only in the presence of supplementary constants, but in the presence of the pH ratio to concentration of the second component of the solution — boric acid.

We conducted experiments of this type at 10 and 50°. Determination of pH, in equilibrium with the solid phase, was by potentiometric titration [3], subsequent to prior determination that slightly soluble compounds in equilibrium are not formed in this situation. This was confirmed by the fact that the pH values for the moment of formation of the solid phase and the equivalent pH values we obtained by the Gromov method, coincided.

Tables 1 and 2 show the results of our experiments. Boric acid activity is always equated to concentration. The data in Tables 1 and 2 were used to plot the $pH-\log a_+$ and $pH-\log C_{H_3BO_3}$ (Figs. 1 and 2).

These figures show that $\dfrac{2x + y}{2y} = 0.5$ and $\dfrac{z}{2y} = 1$.

The former equation gives $x = 0$ and a minimum integer value, $y = 1$.

Combination of the two equations gives $z = 2$. Consequently, the composition of the solid phase is $Ni(OH)_2 \cdot 2H_3BO_3$. It is interesting to note that this formula corresponds to that of the slightly soluble nickel diborate $NiB_2O_4 \cdot xH_2O$ [5].

T A B L E 1

Ratio of pH at Moment of Solid Phase Formation to Activity of Nickel Sulfate in Solution (Concentration H_3BO_3 20 g/l)

Nickel concentration				pH	
(g/l)	(M)	$\gamma_\pm$	$a_\pm$	20°	50°
0.5	0.008	0.425	0.00361	5.22	4.75
1.0	0.017	0.340	0.00578	5.18	4.64
5.0	0.085	0.180	0.01534	4.94	4.44
10	0.170	0.120	0.02045	4.92	4.35
20	0.341	0.075	0.02556	4.88	4.24
30	0.515	0.065	0.03345	4.82	4.26
40	0.681	0.055	0.03748	4.76	4.22
50	0.852	0.050	0.04259	4.64	4.12
60	1.022	0.045	0.04600	4.60	4.04

T A B L E 2

Ratio of pH at Moment of Solid Phase Formation to Concentration of Boric Acid in Solution (Concentration Ni 30 g/l)

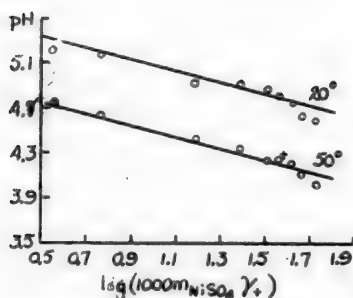| H_3BO_3 concentration		pH	
(g/l)	(M)	20°	50°
2	0.032	5.66	5.06
4	0.064	5.48	4.82
8	0.128	5.18	4.54
12	0.192	4.96	4.36
20	0.323	–	4.20
25	0.404	4.50	4.06
35	0.566	4.44	3.88
45	0.727	4.26	3.73
55	0.889	–	3.60

Fig. 1. Ratio of pH to logarithm of nickel sulfate activity (at 20 and 50° and at a constant concentration of boric acid, 20 g/l). The cross represents data from source [3].
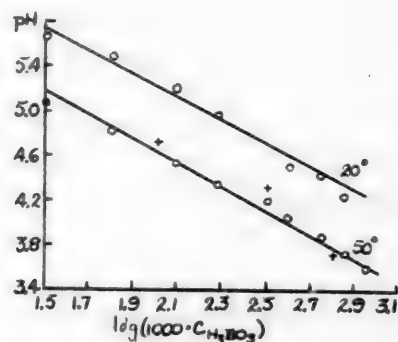
Fig. 2. Ratio of pH to logarithm of boric acid concentration (at 20 and 50° and a constant nickel sulfate concentration, 0.514 M.).

As the solid phase formed is in equilibrium with the solution, the standard isobaric potential of nickel diborate anhydride formation may be computed.

The first series of measurements at 20° provided a value of -55.0 Cal/mole, and the second -54.0 Cal/mole. As the standard isobaric potential of nickel hydroxide formation is -18.9 Cal/mole [1], the standard isobaric potential of association(ΔZ_n^0) of two boric acid moles to one of nickel hydroxide would be -36.1 Cal.

This magnitude is greater than ΔZ_n^0 when nickel sulfate associates with nickel hydrate to form $3NiSO_4 \cdot 4Ni(OH)_2$ (-20.4 Cal [2]), so that when boric acid is present and there is a gradual precipitation of nickel hydroxide, it is nickel diborate that forms to begin with, and not the basic salt.

As may readily be seen from Figs. 1 and 2, the angle coefficients of the straightlines pH-log a do not change with change from 20 to 50°.

This makes it possible to contend that the composition of a slightly soluble compound does not vary with rising temperature. The pH temperature coefficient at the beginning of formation of the solid phase in these experiments is 0.2 pH unit per 10°, which is somewhat lower than previous measurement of this magnitude (0.26 pH unit per 10° [3]).

SUMMARY

1. Potentiometric titration was used to study the composition of the solid phase at the moment of the beginning of its formation, when nickel was precipitated by a base from mixed solutions of nickel sulfate and boric acid.

2. It has been shown that in the entire concentration interval studied, the solid phase, in equilibrium with the solution, consists of nickel diborate $Ni(OH)_2 \cdot 2H_3BO_3$. Basic nickel salts in pseudo equilibrium do not form in the presence of boric acid.

3. Computations of the standard isobaric potentials of nickel diborate formation from ions and from nickel hydroxide and boric acid have been made, and it was demonstrated that the first compound to be formed must be nickel diborate, and not the basic nickel salt.

4. Elevation of temperature to 50° did not change the composition of the solid phase precipitated.

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THE PROBLEM OF ANODE DEPOSITS RESULTING FROM SILVER SALT ELECTROLYSIS. I.

M. S. Skanavi-Grigoryeva and I. L. Shimanovich

Up to the present time the problem of composition and structure of anodic silver deposits resulting from electrolysis of aqueous solutions of its salts on a platinum anode has not been given a final solution.

In the meantime, the anodic deposit is most interesting from a theoretical viewpoint and may have practical utility as a good oxidant, and as starting material for preparation of silver dioxide, and a series of molecular and complex compounds of di- and tri-valent silver.

Deposition of silver compounds upon the anode, along with deposition on the cathode, can also play a role in silver refining, as a substitute for cyanide baths; using the same amount of energy, the silver yield during electrolysis, for example of silver nitrate, with subsequent processing of the anodic deposit, is increased 1.6 - 1.7 fold.

In the present work, the composition, sturcture and conditions for formation of anodic deposits resulting from electrolysis of aqueous solutions of silver nitrate, fluoride, perchlorate, sulfate, chlorate and acetate have been studied.

Conditions for synthesis of anode deposits depend upon the amount of electrolyte used, concentration of the latter, on the form and dimensions of the electrolyzer and the electrodes.

In all case, current density should be such as to ensure only the form of anodic deposit, and no oxygen evolution should be observed.

The authors electrolyzed 1-2 N solutions of the corresponding salt in amounts ranging from 0.25 to 1.0 liter, at a current density from 0.05 to 0.20 A/cm^2. The exception was in the case of silver sulfate solution, for which special conditions are necessary because of its low solubility. In order to avoid dissolution of the anode deposits, electrolysis should be carried out with cooling of the electrolyzer (3-5°), and accumulation of free acid at the anode should not be permitted, as it will cause the deposit to dissolve. To avoid concentration polarization, the electrolyte should be stirred.

During electrolysis of the above-indicated salts, apart from silver acetate, there also formed on the anode well-defined, black crystals, which were quite stable at ordinary temperature, and particularly so in the dark.

From the photographs given (enlarged 200 x), it can be seen that the deposits from nitrate solutions (Fig. 1) and silver fluoride (Fig. 2) crystallize in the form of octahedrons, and from perchlorate (Fig. 3) apparently as cubes. Debye crystallograms were taken of all deposits; a Debye crystallogram of the silver nitrate deposit was confirmed by the data of Zhdanov and Zvonkova [1] for the nitrate deposit lattice. The lattices for solutions of the fluoride and perchlorate deposits were identical with the nitrate lattice. Crystals of these deposits belong to the cubical system and posses a cubic, face-centered lattice with the constants a_{AgNO_3} = 9.87 Å, a_{AgF} = 9.80 Å, a_{AgClO_4} = 9.90 Å.

There are practically no data in the literature [2] on the composition of anodic deposits resulting from silver fluoride, perchlorate, sulfate, chlorate and acetate solutions; there are a sufficient number of works on the study of silver nitrate deposit composition. The composition $2Ag_3O_4 \cdot AgNO_3$ [1,3,4] attributed to this deposit, based upon a large number of analyses, can at the present time be considered as established.

However, there is no uniform answer in the literature with regards to the valency of silver in this compound. Thus, Boky and Smirnova [5] consider, on the basis of crystallochemical analysis, that two types of silver ions are present in this compound: monovalent and divalent. They attribute the formula $4AgO \cdot 2AgO_2 \cdot AgNO_3$ to this deposit, with the presence of two peroxide ions $2(O_2'')$.

The author's data for complete analyses of the anode deposit obtained from silver nitrate are given in Table 1.

The data obtained on percentage composition of the substance composing the deposit, given in Table 1, are confirmed by the following proposed reactions.

Roasting

$$2Ag_3O_4 \cdot AgNO_3 \longrightarrow 7Ag + NO_2 + 9O. \tag{1}$$
$$(79.90\%) \quad (15.24\%)$$

Heating to 165-170°

$$2Ag_3O_4 \cdot AgNO_3 \longrightarrow 3Ag_2O \cdot AgNO_3 + 5O. \tag{2}$$
$$(8.47\%)$$
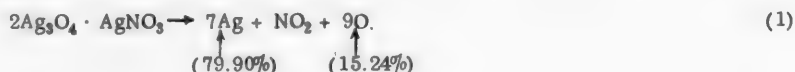
Roasting of the residue after heating at 165-170°

$$3Ag_2O \cdot AgNO_3 \longrightarrow 7Ag + NO_2 + 4O. \tag{3}$$
$$(87.28\%)$$

Heating with hot water

$$2Ag_3O_4 \cdot AgNO_3 \longrightarrow 3Ag_2O_2 + AgNO_3 + 2O. \tag{4}$$
$$(68.49\%) \quad (11.42\%) \quad (3.39\%)$$
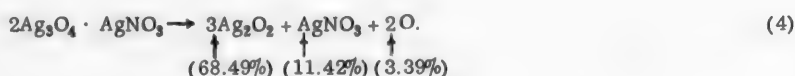
TABLE 1

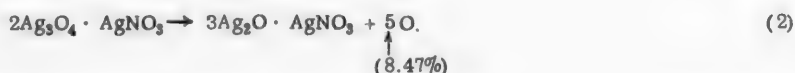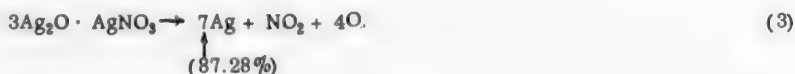| Element being determined	Found (in %)	Calculated (in %)
Total amount of silver	79.90	79.90
Amount of oxygen evolved at 165-170°	8.68	8.47
Amount of oxygen evolved on boiling with water	3.15	3.39
Amount of Ag^+ washed out with hot water	11.39	11.42
Amount of silver in the residue after treatment with hot water	68.67	68.49
Amount of nitrogen	1.41	1.48
Total silver in the residue after removal of oxygen from the higher silver oxides	87.48	87.28
Amount of oxygen evolved on roasting	15.38	15.24
Total amount of oxygen	18.72	18.62
Amount of oxygen involved in oxidation of the oxalic acid	6.75	6.77
Ag_a/Ag_c	0.70	0.70

It can be seen from reactions (2) and (4) that for the compound being investigated, the oxygen present is bound with silver in various ways. The author considers that at 100° (boiling with water, Reaction 4), the oxygen which is bound to trivalent silver is reduced to divalent (known as silver dioxide, Ag_2O_2 [6], stable at 100°). At 165-170°, the oxygen which is bound to di and tri-valent silver is evolved, and the oxide of monovalent silver (Reaction 2) is formed.

The reaction with oxalic acid proved to be of interest. Of the 5 active oxygen atoms in the deposit (8.47%), only 4 (6.77%) participated in the oxalic acid oxidation. If the formula proposed by Boky and Smirnova is adopted, and if it be considered that the oxygen from silver peroxide (AgO_2) participated in the oxidation of oxalic acid, and since silver dioxide does not give constant results in oxalic acid oxidation [7], then the oxidation should go to 2 oxygen atoms if reduction of $2AgO_2$ proceeds to $2AgO$, or 3 oxygen atoms if the reduction proceeds to Ag_2O.

Experiment showed, as indicated above, that 4 oxygen atoms are used for oxidation of the oxalic acid. The authors assume that the composition of the anodic deposit can be represented as a double salt of silver nitrate with the silver salt of the silver acid corresponding to trivalent silver, similar to that for the gold acid, $HAuO_2$, namely $2Ag^{II}(Ag^{III}O_2)_2 \cdot AgNO_3$. In such case, only trivalent silver should participate in the oxidation of oxalic acid, and reaction should proceed according to the acheme:

$$2Ag(AgO_2)_2 + 2H_2C_2O_4 \longrightarrow 2AgC_2O_4 + 4HAgO_2$$
$$(2H_2O + 2Ag_2O_3)$$

$$2Ag_2O_3 + 2H_2C_2O_4 \longrightarrow 2Ag_2C_2O_4 + 4O + 2H_2O$$

$$\frac{4H_2C_2O_4 + 4O \longrightarrow 8CO_2 + 4H_2O}{2Ag(AgO_2)_2 + 8H_2C_2O_4 \longrightarrow 2AgC_2O_4 + 2Ag_2C_2O_4 + 8CO_2 + 8H_2O}$$
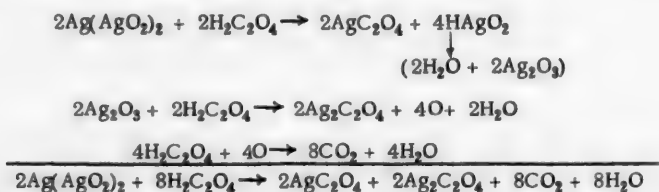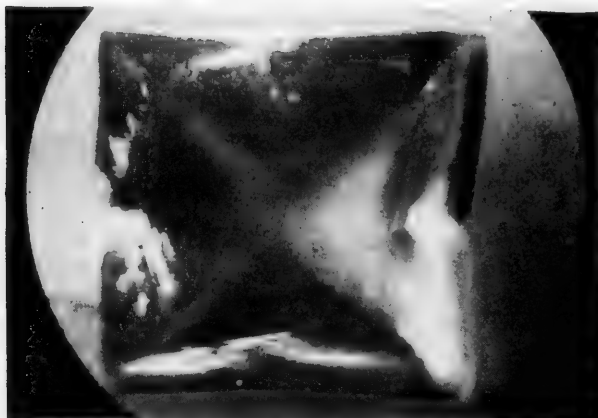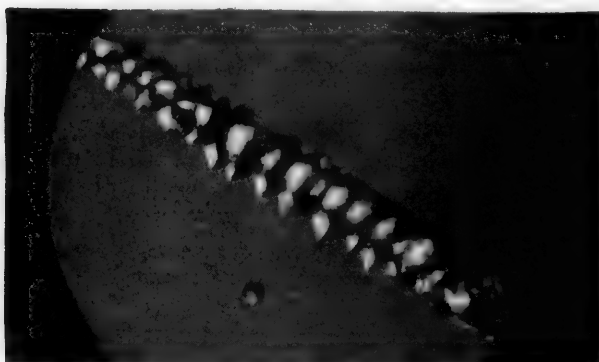
Fig. 1. Deposit from AgNO$_3$ solution.

Fig. 2. Deposit from AgF solution.
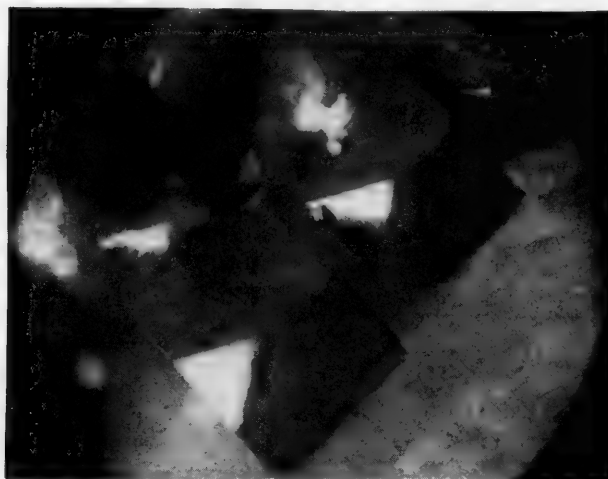

Fig. 3. Deposit from AgClO$_4$ solution.

with formation of mono- or of divalent silver oxalate. The existence of AgC_2O_4 is quite possible, by analogy with $Ag(CH_3COO)_2$ [8].

From a determination of the composition and the proposed structure for silver compounds being deposited upon the anode, the authors have proposed a method for determination of the ratio between the amount of silver which goes into the composition of the anode deposit (Ag_a) and the amount of silver being deposited within the same time on the cathode (Ag_c). This ratio should be determined only in those cases where a deposit is formed only on the anode, and no oxygen evolution is observed.

If the composition $2Ag(AgO_2)_2 \cdot AgNO_3$ is attributed to the deposit on the anode, then the monovalent silver should go into the anode as divalent and trivalent; furthermore, if the anode deposit does indeed correspond to the above given formula, and 2 divalent silver atoms and 4 trivalent silver atoms are found in it, then the total loss of electrons by silver upon its oxidation on the anode is equal to 10.

$$2Ag^+ \xrightarrow{-2e} 2Ag^{++}$$

$$\frac{4Ag^+ \xrightarrow{-8e} 4Ag^{+++}}{\text{Total } -10 \text{ e}}$$
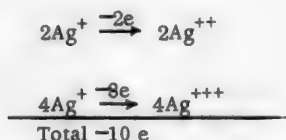
Since the anode has accepted 10 electrons, the cathode therefore should give up the same number of electrons, i.e., 10 atoms of silver should be deposited on the cathode.

$$10Ag^+ + 10e \longrightarrow 10Ag^0.$$

Hence the ratio of anodic silver to cathodic silver, Ag_a / Ag_c should be equal to 0.70. With a large number of experiments, the authors were able to confirm this ratio for silver nitrate.

The authors used a similar method of calculation for determination of the composition of anodic deposit resulting from silver fluoride. The ratio of Ag_a / Ag_c was found equal to 0.70; it follows thus that the formula $4Ag_3O_4 \cdot 3AgF$ proposed by Tanatar [9] is not accurate because with such a formula this ratio should be equal to 0.75 and the total content of silver should constitute 83.79% and not 79.60%, as the experiment indicated.

TABLE 2

Element determined	Found (in %)	Calculated (in %)
Total amount of silver	79.60	79.56
Fluoride	3.97	4.00
Total amount of oxygen	13.28	13.48
Amount of oxygen evolved on heating to 135-140°	8.41	8.43
Amount of silver in the deposit after heating deposit at 135-140°	86.72	86.98
Amount of water of crystallization	2.68	2.85
Amount of oxygen participating in oxidation of the oxalic acid	6.73	6.74
Ag_a / Ag_c	0.70	0.70

Data on determination of the individual elements in this compound (Table 2), which were not given by Tanatar, made it possible for the authors to attribute the formula $2Ag(AgO_2)_2 \cdot AgF \cdot HF \cdot 1\frac{1}{2}H_2O$ to this compound.

By investigating the crystals obtained from silver perchlorate via the same methods as were used with the nitrate and fluoride, the authors came to the conclusion (Table 3) that they should have the formula $2Ag_3O_4 \cdot AgClO_4$.

Heating at 125-130°.

$$2Ag_3O_4 \cdot AgClO_4 \longrightarrow 3Ag_2O \cdot AgClO_4 + \underset{(8.14\%)}{5O}.$$

Heating with hot water

$$2Ag_3O_4 \cdot AgClO_4 \longrightarrow \underset{(65.87\%)}{3Ag_2O_2} + \underset{(10.98\%)}{AgClO_4} + \underset{(3.26\%)}{2O}.$$
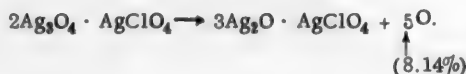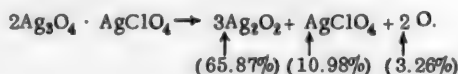
TABLE 3

Element determined	Found (in %)	Calculated (in %)
Total amount of silver	76.80	76.85
Amount of oxygen evolved at 125-130°	8.22	8.14
Amount of silver (Ag^+) washed out with hot water	10.99	10.98
Amount of silver in residue after treatment with hot water	65.56	65.87
Amount of oxygen evolved upon boiling with water	3.10	3.26
Ag_a / Ag_c	0.70	0.70

The oxidation reaction of oxalic acid indicates for oxidation of the latter, that 4 oxygen atoms are not used, as might have been expected by analogy with nitrate and fluoride deposits, but instead, 3 oxygen atoms. Evidently the anodic deposit from perchlorate possesses a somewhat different structure, as evidenced by its different crystalline form as well.

SUMMARY

1. Upon electrolyzing aqueous solutions of silver nitrate, fluoride and perchlorate on a platinum anode, crystalline black deposits, with metallic lustre are formed, stable at normal temperature.

2. The use of a method for determining the ratio of silver entering into composition of the anodic deposit to the amount of silver being deposited within the same period at the cathode has been proposed the authors, and a detailed chemical investigation of the deposits has allowed them to make a proposal of the following formula for these substances:

1. $2Ag(AgO_2)_2 \cdot AgNO_3$,

2. $2Ag(AgO_2)_2 \cdot AgF \cdot HF \cdot 1\frac{1}{2}H_2O$,

3. $2Ag_3O_4 \cdot AgClO_4$.

3. Crystals of the resulting deposit belong to the cubical system, possess a cubic face-centered cell, with the constants for nitrate deposit of 9.87 Å, for fluoride of 9.80 Å, and for perchlorate 9.90 Å.

4. The composition of the anodic deposits does not depend upon the current density, the electrolyte concentration, or the temperature, under those conditions of electrolysis where there is formed only the deposit at the anode, and no other reactions occur.

5. The ratio of Ag_a / Ag_c under those anodic conditions where only a deposit is formed is equal to 0.7 for the deposits.

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NIOBATES AND TANTALATES OF THE ALKALI EARTH METALS. II.

V. A. Pchelkin, A. F. Efimov and A. V. Lapitsky

The literature describes a relatively small number of aqueous salts of the niobium and tantalum acids; they include the hexaniobates of lithium [1,3], sodium and potassium [2], and also the hexatantalates of sodium and potassium [4]. In addition to the foregoing salts, there are references to barium hexaniobate $Ba_7Nb_{12}O_{37} \cdot 18H_2O$ [2], and barium hexatantalate $Ba_4Ta_6O_{19} \cdot 6H_2O$ [6], having been found.

We have obtained the hexaniobates and hexatantalates of all the alkali earth metals, although the majority of them had never been described previously in the literature.

EXPERIMENTAL

1. Initial Materials

Niobium pentoxide and tantalum pentoxide. To obtain the hexaniobates and hexatantalates of the alkali earth metals we made use of pure niobium and tantalum pentoxides, separated out and purified by the methods we described in a series of communications [5,6,7].

Sodium hexaniobate, $Na_{14}Nb_{12}O_{37} \cdot 32H_2O$. 8 g calcined niobium pentoxide were fused in a silver cup with 32 g caustic soda. After cooling, the resultant melt was pulverized and washed with water to remove the excess caustic soda. The salt residue $Na_{14}Nb_{12}O_{37} \cdot 32H_2O$ was dissolved in water while heated, filtered and concentrated to a small volume. After the addition of an equal volume of alcohol, a residue of sodium hexaniobate was precipitated out. The salt was filtered and washed with alcohol and ether. Analysis showed the salt thus obtained to have the composition: $Na_{14}Nb_{12}O_{37} \cdot 32H_2O$.

Potassium hexatantalate $K_{16}Ta_{12}O_{31} \cdot 33H_2O$. 10 g tantalum pentoxide were fused with 30 g pulverized caustic potash, water then being used to remove the excess alkali from the melt. The salt residue was filtered, washed with alcohol and dissolved in water, the solution then filtered and concentrated to half its volume. The addition of an equal volume of alcohol resulted in the precipitation of potassium hexatantalate. The composition of the salt was confirmed by analysis.

2. Preparation of the Hexaniobates and Hexatantalates of the Alkali Earth Metals

Hexaniobates of the alkali earth metals. These salts were obtained by adding nitrates of calcium, strontium and barium (chem. pure) to sodium hexaniobate solution. It was noted that the rate of formation of precipitates varied. The barium salt was the most rapidly precipitated, and the calcium — the most slowly. The salts obtained were analyzed for metallic oxide, niobium pentoxide, and water content. The metallic oxide was determined as the sulfate, while the niobium pentoxide — as usual [5]. The water content was arrived at by the determination of constant weight upon the calcination of the salt samples. The results of chemical analysis of the hexaniobates of the alkali earth metals follow.

Analysis of calcium hexaniobate.

Sample of substance 0.2734 and 0.2056 g.
Found %: CaO 15.08, 15.14; Nb_2O_5 63.74, 63.88; H_2O 21.00, 20.94. $Ca_7Nb_{12}O_{37} \cdot 30 H_2O$. Calculated %: CaO 15.29; Nb_2O_5 63.68; H_2O 21.03.

Analysis of strontium hexaniobate.

Sample of substance 0.2830 and 0.2247 g.
Found %: SrO 25.68, 25.34; Nb_2O_5 56.24, 56.62; H_2O 18.04, 18.30. $Sr_7Nb_{12}O_{37} \cdot 29 H_2O$. Calculated %: SrO 25.50; Nb_2O_5 56.08; H_2O 18.42.

Analysis of barium hexaniobate.

Sample of substance 0.2166 and 0.2454 g.

Found %: BaO 33 70, 33.38; Nb_2O_5 49.52, 49.8C; H_2O 16.60, 16.94. $Ba_7Nb_{12}O_{37} \cdot 30H_2O$. Calculated %: BaO 33.4C; Nb_2O_5 49.71; H_2O 16.83.

The analytical results show that exchange reactions between nitrates of the alkali earth metals and sodium hexaniobate result in salts of the following composition:

$$Ca_7Nb_{12}O_{37} \cdot 30H_2O, \; Sr_7Nb_{12}O_{37} \cdot 29 H_2O, \; Ba_7Nb_{12}O_{37} \cdot 30H_2O.$$

Hexatantalates of the alkali earth metals. These salts were obtained in the same manner as in the previous case. The hexatantalates of calcium, strontium and barium formed by the reaction of the corresponding nitrate with sodium hexatantalate, were gelatinous white precipitates. The precipitates were filtered, carefully washed with water and air-dried to a constant weight.

Results of analysis of the salts follow.

Analysis of calcium hexatantalate

Sample of substance 0.1862 and 0.3208 g.

Found %: CaO 12.30, 12.23; Ta_2O_5 71.16, 71.88; H_2O 16.11, 16.04. $Ca_8Ta_{12}O_{38} \cdot 33H_2O$. Calculated %: CaO 12.12; Ta_2O_5 71.91; H_2O 15.97.

Analysis of strontium hexatantalate

Sample of substance 0.2502 and 0.2480 g.

Found %: SrO 20.53, 21.12; Ta_2O_5 65.52, 64.59; H_2O 14.44, 14.11. $Sr_8Ta_{12}O_{38} \cdot 33 H_2O$. Calculated %: SrO 20.40; Ta_2O_5 65.03; H_2O 14.57.

Analysis of barium hexatantalate

Sample of substance 0.2238 and 0.3116 g.

Found %: BaO 27.34, 27.08; Ta_2O_5 59.60, 59.29; H_2O 13.06, 13.42. $Ba_8Ta_{12}O_{38} \cdot 33H_2O$. Calculated %: BaO 27.38; Ta_2O_5 59.33; H_2O 13.29.

The data show that we obtained the hexatantalates of calcium: ($Ca_8Ta_{12}O_{38} \cdot 33H_2O$), strontium ($Sr_8Ta_{12}O_{38} \cdot 33H_2O$) and barium ($Ba_8Ta_{12}O_{38} \cdot 33 H_2O$).

Conductometric titration. Conductometric titration was undertaken for quantitative verification of exchange reaction results in preparing the hexaniobates and hexatantalates of the alkali earth metals. Some changes were made in the usual design of the apparatus for determining the electrical conductivity of a solution: the Wheatstone bridge was replaced by two resistance boxes, and an oscillograph took the place of the headphones used to determine the sound minimum. The end of the exchange reaction was determined when minimum amplitude of oscillation was reached.

Titration curve minimums noted in all cases confirmed simple replacement of base metal by alkali earth in hexaniobate and hexatantalate without change in oxide relationships in salt molecules, representing a verification of the chemical analysis results.

Determination of alkali earth metal hexaniobate and hexatantalate saturated solution electrical conductivity. As the salts obtained were of weak solubility, we decided to determine the specific conductivity of saturated solutions of all the compounds we had derived.

Determination of alkali earth metal metaniobate and metatantalate saturated solution electrical conductivity was performed by means of a conductometric titration apparatus at 20°.

A bi-distillate• was used to prepare saturated solutions of the salts under investigation. Each value for specific conductivity adduced in the table represents an average of 3 or 4 measurements.

The absence of data on the mobility of the $Nb_{12}O_{37}^{-}$ [14] and $Ta_{12}O_{38}^{-}$ [16] ions in the literature made it impossible to compute the solubility values of these salts.

Air-dried hexaniobates of calcium, strontium and barium and hexatantalates of calcium, strontium and barium were subjected to roentgenographic study by means of powdergrams. All the radiograms showed an absence of lines, permitting the conclusion that these compounds are roentgenamorphous. After calcination at temperatures over 400°

• The specific conductivity of the bi-distillate was $1.4 \cdot 10^{-6}$ ohm^{-1} am^{-1} .

TABLE

Specific Electrical Conductivity of Alkali Earth Metal Metaniobate and Metatantalate Saturated Solutions at 20°
(beaker constant 0.4439)

Compound	Electrical conductivity	
	Equivalent	Specific
$Ca_7Nb_{12}O_{37} \cdot 30H_2O$	$5.8 \cdot 10^{-5}$	$2.6 \cdot 10^{-5}$
$Sr_7Nb_{12}O_{37} \cdot 29H_2O$	$1.85 \cdot 10^{-5}$	$8.2 \cdot 10^{-6}$
$Ba_7Nb_{12}O_{37} \cdot 30H_2O$	$2.00 \cdot 10^{-5}$	$9.0 \cdot 10^{-6}$
$Ca_8Ta_{12}O_{38} \cdot 33H_2O$	$1.84 \cdot 10^{-5}$	$8.19 \cdot 10^{-6}$
$Sr_8Ta_{12}O_{38} \cdot 33H_2O$	$1.72 \cdot 10^{-5}$	$7.62 \cdot 10^{-6}$
$Ba_8Ta_{12}O_{38} \cdot 33H_2O$	$1.43 \cdot 10^{-5}$	$6.39 \cdot 10^{-6}$

samples of all salts under study showed clearly defined lines coinciding completely with the lines of alkali earth metals, anhydrous metaniobates and metatantalates, indicating the decomposition of these salts upon heating.

SUMMARY

1. The hexaniobates of calcium and strontium, and hexatantalates of calcium, strontium and barium were produced for the first time.

2. The specific electrical conductivity of solutions, saturated at 20°, of hexaniobates and hexatantalates of all the alkali earth metals, was determined.

3. It was shown that alkali earth metal hexaniobates and hexatantalates are thermally unstable at temperatures over 400°.

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FACTORS DETERMINING STABILITY OF CERTAIN TYPES OF COMPLEX COMPOUNDS IN AQUEOUS SOLUTIONS

K. B. Yatsimirksy

There has accumulated during the last few years quite a significant amount of material on the stability of complex compounds in aqueous solutions. Instability constants have been determined for 700-800 complex ions. The existence of such a tremendous mass of factual material makes it possible to pose the question of elucidation of factors determining stability of the groups of complex compounds which have received the most study. Those complex compounds are considered whose central atoms can form stable hydrated ions (complex compounds of silver, copper, aluminum and other metals). Complex compounds of platinum, gold antimony, tetravalent lead, and some of the platinum group metals, on dissociation in aqueous solutions, do not form hydrated ions and are not considered in this paper.

For complex compounds forming hydrated ions upon dissociation, the chemical bond approximates the ionic type, the central atom preserving the properties of the ions to a considerable extent, and in such cases central atoms can be mentioned as well as central ions.

The stability of complex compounds with some additives, for the cases investigated, is determined by such characteristics of the central ions as charge, radius, and its polarizability (ability to deform the electronic shell of the additive atoms, with tendency to covalent bond formation). To clarify the role of various factors, it was expedient to investigate a group of complex ions with the same additives in which only one characteristic of the central ions is changing (charge, radius or polarizing action), and two others of approximately the same stability.[•]

In order to elucidate the effect of charge upon the stability of complex compounds, three sets of cations of approximately the same dimensions were chosen: 1) Na^+, Ca^{2+}, Y^{3+}, Th^{4+} (cation radius $r_c = 1.04 \pm 0.06$ A), 2) K^+, Sr^{2+}, La^{3+} ($r_c = 1.27 \pm 0.06$ A) and 3) Ag^+, Hg^{2+}, Tl^{3+} ($r_c = 1.09 \pm 0.04$ A).

In the first two sets, the cations possess a complete shell of eight electrons and low oxidizing potential, and in the third set the cations possess a shell of eighteen electrons, with approximately the same oxidizing potential (about 0.8 v.). It can be assumed that in a related series the polarizing action of the cations is approximately the same.

In Table 1 are given values for the indices of instability constants ($pK = -\log K_{instab.}$) for the three series of ions. In almost all cases, pK increases with increase in charge. Particularly noticeable is the increase in pK with low or highly charged additives. The stability of complexes with large amounts of additives of low charge changes but little with a change in charge of the central ion (complex iodides, bromides, nitrates, and others).

The change in pK with charge in charge proceeds so regularly that in some cases interpolation is possible. Thus, for example, values for the instability constant indices of nitrate and iodate complexes of yttrium can be evaluated: For YNO_3^{2+} $pK = 0.45 \pm 0.07$, for YIO_3^{2+} $pK = 1.9 \pm 0.3$.

To clarify the effects of other factors upon the stability of complex compounds, we might examine a little more closely the function which the author, together with Grinberg, developed [4]. It was demonstrated that the thermal effect of MA_n complex formation in aqueous solutions of a central ion, M, and additive, A, can be represented by the following equation:

$$\Delta H = W_{aq} - W_c + const_1. \tag{1}$$

where W_{aq} and W_c = respectively, the energy of addition of nH_2O molecules and n particles of A to the central ion. It was indicated earlier [5] that the energy of addition can be presented as a sum of two factors: the energy of electrostatic attraction (W^i) and the polarization energy (P). Equation (1) can therefore be modified in the following manner:

$$\Delta H = W_{aq}^i - W_c^i + P_{aq} - P_c, + const_1. \tag{2}$$

• Values for instability constants are taken from the author's review article [1] and other reviews [2,3].

T A B L E 1

Indices of Instability Constants for a Series of Ions with Alternating Charge

Types of complex ions	pK for the charge of the central ions (Z)			
	+1	+2	+3	+4
	K^+ Sr^{2+} La^{3+}			
ROH^{Z-1}	(−0.7)	1.0	3.3	-
$RS_2O_3^{Z-2}$	0.1	2.0	-	-
$RP_3O_9^{Z-3}$	1.2	3.4	5.7	-
$RFe(CN)_6^{Z-3}$	1.2	2.8	3.7	-
	Na^+, Ca^{2+}, Y^{3+}, Th^{4+}			
RIO_3^{Z-1}	-	0.9	-	2.9
RNO_3^{Z-1}	-	0.3	-	0.6
RSO_4^{Z-2}	0.7	2.3	3.5	4.1
$RC_2O_4^{Z-2}$	-	3.0	7.3	-
$REdta^{Z-4}$ *	-	11.1	18.0	-
	Ag^+, Hg^{2+}, Ti^{3+}			
ROH^{Z-1}	2.3	10.3	14.8	-
RNH_3^{Z}	3.2	8.8	-	-
RCl^{Z-1}	2.7	5.3	8.1	-
RBr^{Z-1}	9	9.1	9.7	-

The polarization energy is calculated by means of an empirical equation of the type

$$P = n\beta a \rho \qquad (3)$$

where a = polarizability of the additives, ρ = polarizing action of the cation, β = a coefficient, being determined by the additive dimensions and those of the central ion. Whereupon,

$$P_C - P_{aq} = n(\beta_c a_A - \beta_{aq} a_{H_2O})\rho, \qquad (4)$$

The value in parentheses is related to the relative polarizability of additive A, and will be symbolized as b'. The b' value depends not only upon the ratio between the polarizabilities of the additive and of the water (a_A and a_{H_2O}), but also depends upon the dimensions of the central ions and of the additives.

For acid complexes, we then have

$$\Delta H = \frac{A}{(r + r_W)^2} - \frac{B}{r + r_A} - nb'\rho + const_1, \qquad (5)$$

where r, r_A and r_W = the radii, respectively, of the central ion, the anion-additive and a water molecule, and A and B = constants, determined by the charges (or by the dipole moments) of the reacting particles and by the spatial configuration of the complex.

In the case of monotypical complexes, entropy change for the reaction in question fluctuates within a comparatively small range [6], and therefore a simple function exists between the instability constant and ΔH

$$RT \ln K_{inst.} \approx \Delta H + const_2. \qquad (6)$$

If a series of complexes is selected with an approximately constant polarization energy, then the effect of radius upon the ΔH value can be revealed, and as a consequence of which, the stability of the complexes. For this purpose, Equation (5) can be differentiated

$$\frac{\partial \Delta H}{\partial r} = \frac{B}{(r + r_A)^2} - \frac{2A}{(r + r_W)^3}. \qquad (7)$$

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* Edta = ethylenediaminetetracetate.

It follows from Equation (7) that with an increase in cation radius, the stability of the complexes may increase (if the first member of the first part of the equation is smaller than the second), decrease, and pass through a maximum. An increase in stability of the complexes with increase in cation radius should be observed in the case of anion-additives of high radius values (r_A), and, contrariwise, for the case of small anions, the stability of complexes should decrease with an increase in cation radius.
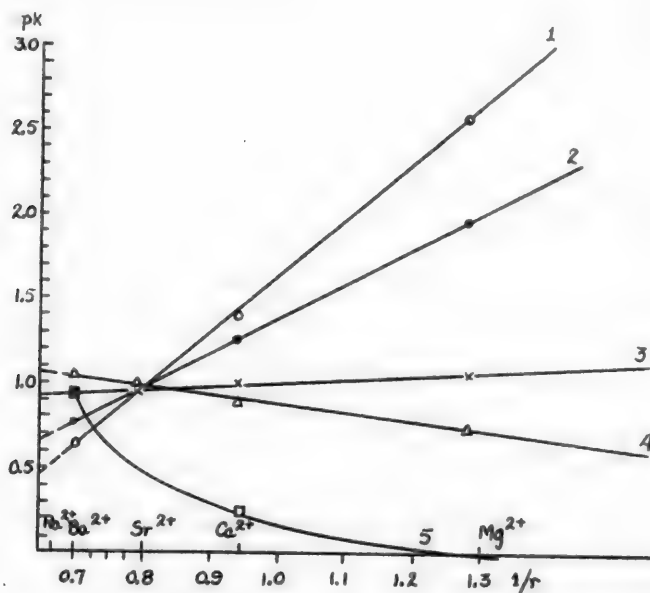
Fig. 1. Instability constant indices for a series of doubly -charged ions of varying radius.
1) MOH^+ (r_A = 1.40), 2) $MAlan^+$, 3) $MCH_3CO_2^+$ (r_A = 1.59), 4) MIO_3^+ (r_A = 1.82), 5) RNO_3^+ (r_A = 1.89).

These views are confirmed by extensive experimental material. In Figs. 1 and 2 there is shown the change in stability of complex ions formed from elements of the second main group of the Mendeleev periodic system. In the case of small singly-charged ions (r_A < 1.6 A) and a -aminoacids, the stability of the complexes changes continuously from Mg^{++} to Ba^{++}. If the radius of the anion-additive exceeds 1.6 A (nitrates, iodates) then the stability of the complex compound changes in reverse order. Apparently the same rules are observed also by doubly-charged anion-additives; stability of the oxalate complexes increases with decrease in radius, stability of succinate complexes being almost independent of the cation radius value, and finally, stability of thiosulfate complexes increasing with increase in radius. Indices for the instability constant of complexes with triply- and quadruply-charged anion-additives either do not change with change in radius, or pass through a maximum.

The mechanisms found here can be utilized to control data on stability of complex compounds, the values for certain constants being found by interpolation, and possibly by extrapolation. Such extrapolation is quite permissible according to data indicated by Shubert and other investigators[7,8].

Sulfate complexes of magnesium and calcium have approximately the same stability (pK = 2.3 ± 0.1). The sulfate ion radius = 2.30 A. Utilizing the mechanisms developed here, the author has assumed that barium and strontium also form sulfate complexes with instability constants equal to 2.3 ± 0.2 for $BaSO_4$ and $SrSO_4$. From this point of view the dissolution of $BaSO_4$ in concentrated H_2SO_4 can be explained not only by formation of an acid salt, but also by formation of a complex of the type $Ba(SO_4)_2^{2-}$.

There are no data in the literature pertaining to calcium pyrophosphate complexes, but the existance of magnesium pyrophosphate complexes has been proved [9]. Since the pyrophosphate ion charge is high, and its dimensions considerable, the existence of such complexes can be demonstrated by direct qualitative experiment: the precipitate of calcium pyrophosphate dissolved readily in excess sodium pyrophosphate.

For monotypical complex compounds, formed from ions of the same charge and of approximately the same volume, the following relationship is derived from Equations (5) and (6):

$$pK = a' + nb\rho, \qquad (8)$$

where $a' = a$ constant, including many values which do not change for a series of isochoric ions, and $b = b'/RT$, signifying the relative polarizability of the additive.

The following can be given as examples of the group of isochoric ions: Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}. There is preserved in this series a constant change in complex stability with any of the additives. This observation has been made by a number of investigators [4,10,11]; copius material confirming this rule has been given by Irving and Williams [3]. Upon filling one or two coordination positions in the internal sphere, stability of the complexes in this series increases in the following order: Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}. With a large number of monomial additives, the order indicated may be slightly out of line.

Continuity in change of stability for various complexes in a series of isochoric ions is explainable by the fact that only one characteristic is changed (polarizing action of the cation), the remaining being constant. For complexes with a given group of additives, there can be observed a change in stability of a determined order among ions of various radii [1,6]. However, with other additives of the series
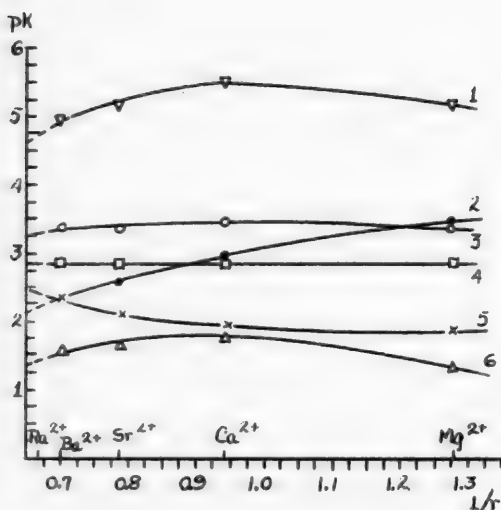

Fig. 2. Indices for instability constants for a series of doubly-charged ions with varying radii.

1) $MP_4O_{12}^{2-}$, 2) $MP_3O_9^-$, 3) MC_2O_4, 4) $MFe(CN)_6^-$, 5) MS_2O_3, 6) $MC_4H_4O_4$.

indicated, transpositions can be observed in similar fashion when an attempt is made to put into the investigated series non-isochoric ions (for example Pb^{2+} and Cd^{2+}).

Equation (8) can be utailized with that data on hand with respect to relative polarizability of additives (b), and polarizing action of the cations (ρ). A number of investigators have related the polarizing action of ions with ionization potential values [5,6,10,11]. Such dependence of course exists, but is observed only approximately, and only for isochoric ions. This dependence can be utilized only for qualitative comparisons of stability change in the series quoted.

For development of quantitative relations, the author will utilize conditional values for relative polarizability of additives, taking the polarizability of alaninate (a-aminopropionate) as equal to unity. The course of subsequent deliberations will not be altered if alaninate polarizability be taken as equal to any other constant value, or if some otner additive is selected as a standard of polarizability. Choice of alaninate as the standard of polarizability was motivated by the fact that agreement in values for alaninate instability constants were independently arrived at by several investigators [12,13]. From Equation (8) one obtains

$$\rho = pK_1^0 - a', \qquad (9)$$

where $pK_1^0 = $ index for instability of complexes of the type $MCH_3CHNH_2COO^+$ (abbreviated further to $MAlan^+$). By means of these values, as can be seen, the polarizing action for cations of the series investigated can be expressed. The pK_1^0 values are given as follows: Mg^{2+} 2.0, Mn^{2+} 3.0, Fe^{2+} 4.0,* Co^{2+} 4.8, Zn^{2+} 5.2, Ni^{2+} 6.0, Cu^{2+} 8.5.

From Equations (8) and (9) one obtains

$$pK = a + nb\,pK_1^0, \qquad (10)$$

where $a = a'(1 - nb_.)$.

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* Interpolated value

1488

Equation (10) is used for complex compounds of the type MA and MA_2 for the cases of ammoniates, alaninates, glycinates and glycylglycinates. Upon adding one particle of additive, Equation (10) is used for complexes with ethylenediamine, propylenediamine, diethylenetriamine, acetate, oxalate, malonate, succinate, hydroxyl, salicylic and sulfosalicylic aldehydes, thiosulfate, trimetaphosphate, tetrametaphosphate, iminodiacetate, iminodipropionate, iminopropionoacetate, hydroxy-ethyliminoacetate, oxyquinolate and dioxydiethylglycinate. Thus, Equation (10) has been checked on 27 series of complex compounds, certain examples being given in Figs. 3 and 4. Average deviations in pK values amount to $\pm$ 0.15.

In the cases investigated, all instability constant indices for a series of isochoric ions are related to each other by a direct linear function.
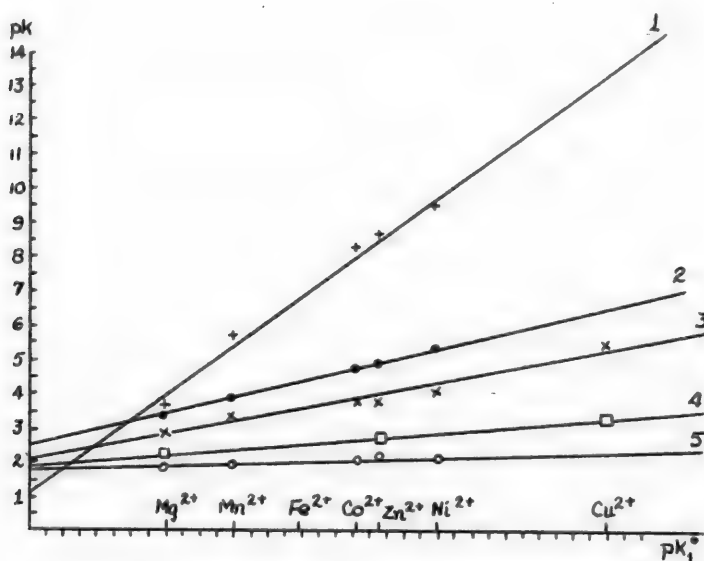
Fig. 3. Indices for instability constants in a series of isochoric ions.
1) $M[HOC_2H_4N(CH_2CO_2)_2]$, 2) MC_2O_4, 3) $MCH_2(CO_2)_2$, 4) $M(CH_2CO_2)_2$, 5) MS_2O_3.

Equation (10) is not observed, however, if more than two nitrogen or oxygen atoms enter into the internal sphere. Deviations in linear function are observed in the case of ammoniacal complexes containing more than two ammonia molecules, ethylenediamine complexes with two or more molecules of ethylenediamine, as well as with complexes of ethylenediaminotetraacetate, nitrilotriacetate and other similar additives; nevertheless, there exists in these cases a linear relationship between the indices for instability constants within a related group of complex compounds.

Constants for Equation (10) for various groups of complexes are given in Table 2; relative polarizability of additives has been calculated through a tangent of the angle of slope for the straight line, $pK - pK_1^0$.

Relative polarizability of additives is determined by the nature of the atoms, by which there is obtained a relationship between the central atoms (the lowest values for b are for additives bound to oxygen; average value — for amino acids (bound through O and N); highest b values are characteristic of additives bound to the central atom through nitrogen).

The linear functions revealed between indices for instability constants can be used as control for data at hand. For examples, we might quote data for $CoOH^+$, published in the same year and same journal. According to Gayer and Woontner [14], the pK = 1.8, and according to Chaberek, Courtney and Martell [15], the pK for $CoOH^+$ is 5.1. According to Equation (10), utilizing the constants given in Table 2, the pK is 4.4.

The linear function found can also be utilized to calculate an unknown instability constant by interpolation or extrapolation. In Table 2 there are given constants of Equation 10 for 27 series of complex compounds calc. from 128 values for instability constants. Instability constant values are not known for 61 complexes, but can be evaluated to an

accuracy of $\pm$ 0.3, the constants being given in Table. 2
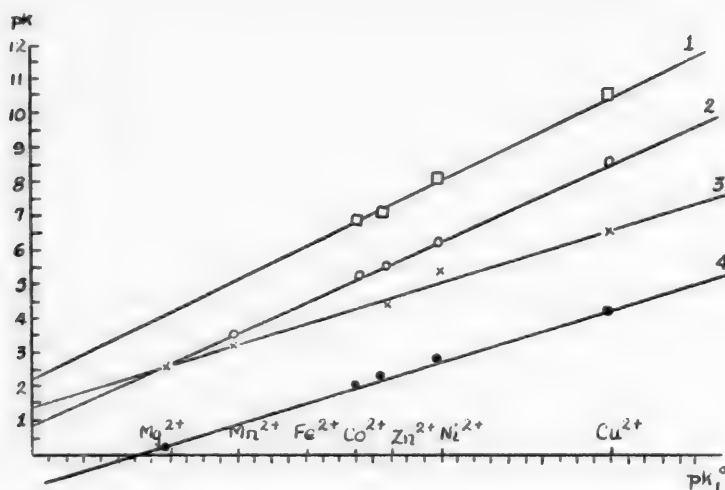
Fig. 4. Indices for instability constants in a series of isochoric ions.
1) $MP_4O_{12}^{2-}$, 2) $MP_2O_9^-$, 3) MC_2O_4, 4) $MFe(CN)_6^-$, 5) MS_2O_3, 6) $MC_4H_4O_6$.

TABLE 2

Equation (10) constant for complexes with doubly-charged isochoric ions (radius 0.8-0.9 A)

Additive	No.of addi-tives	a	Rela-tive polar-izabil-ity	Additive	No of addi-tives	a	Rela-tive polar-izabil-ity
SO_4^{2-}	1	2.35	0.00	o-oxyquinolate	1	5.0	0.96
$P_3O_9^{3-}$	1	3.4	0.00	$(OHC_2H_4)_2NCH_2CO_2^-$	1	0.4	0.96
$P_4O_{12}^{4-}$	1	5.2	0.00	$H_2NCH_2CO_2^-$	1	0.9	0.90
$S_2O_3^{2-}$	1	1.8	0.06	$H_2NCH_2CO_2^-$	2	0.4	0.90
$CH_3CO_2^-$	1	0.7	0.18	$CH_3CHNH_2CO_2^-$	2	−1.0	1.00
$(CH_2CO_2)_2^{2-}$	1	1.8	0.18	$HN{<}^{CH_2CO_2^-}_{C_2H_4CO_2^-}$	1	0.5	1.12
$CH_2(CO_2)_2^{2-}$	1	2.0	0.41				
$C_2O_4^{2-}$	1	2.5	0.47	$HN(C_2H_4CO_2)_2^{2-}$	1	−0.8	1.19
$C_6H_3{<}^{CHO}_{\substack{SO_3^- \\ O^-}}$	1	0.0	0.62	$HN(CH_2CO_2)_2^{2-}$	1	2.2	0.97
				$HOC_2H_4N(CH_2CO_2)_2^{2-}$	1	1.1	1.44
				NH_3	1	−1.0	0.61
$C_6H_4{<}^{CHO}_{O^-}$	1	1.5	0.67	NH_3	2	−2.2	0.59
OH^-	1	1.4	0.62	$C_2H_4(NH_2)_2$	1	−1.7	1.44
$NH_2CH_2COHNCH_2COO^-$ (glycyl-glycinate)	1	−0.2	0.76	$CH_3C_2H_3(NH_2)_2$	1	−1.7	1.44
$NH_2CH_2CONHCH_2COO^-$	2	−2.0	0.80	diethylenetriamine	1	−3.0	2.3

Some examples of such an evaluation of instability constants for ammoniacal, ethylenediamine, sulfate, thiosulfate, acetate and oxalate complexes are given in Table 3. Instability constants can be evaluated in a number of other cases by similar procedure.

The linear function for pK, as revealed by the author, can be used to predict the possibility of existence of new complexes and for evaluation of their stability. If a complex compound of given type is found in solution for magnes-

ium, copper, and one other intermediate member of the series, and in such case the presence of a linear function between the pK's has been established, then there should also exist for the four remaining ions a complex compound of the type in question, and instability constant values for them can be determined by interpolation.

TABLE 3
Calculated instability constant values for certain complexes

Complex ion	pK	Complex ion	pK
$MnNH_3^{2+}$	0.8	$FeOH^+$	3.9
$Mn(NH_3)_2^{2+}$	1.3	$CoOH^+$	4.4
$FeNH_3^{2+}$	1.4	$MnCH_3COO^+$	1.2
$Fe(NH_3)_2^{2+}$	2.2	$FeCH_3CO_2^+$	1.4
$FeSO_4$	2.3	$NiCH_3CO_2^+$	1.8
FeS_2O_3	2.0	CuC_2O_4	6.5
FeC_2O_4	4.4	$MgC_2H_4(NH_2)_2^{2+}$	1.2

The question of the nature of additive effect upon stability of the complex compounds is found to be somewhat more complicated. The value of the additive charge (stabilization of the complex with increase in additive charge), its dimensions and polarizability play an important role, determined in first approximation by the nature of the atoms entering into the internal sphere. The entropy factor plays a considerable role in this case, since the entropy change fluctuates within a wide range, depending upon the nature and number of additives.

SUMMARY

1. The stability of complexes in aqueous solution increases with an increase in charge of the central ion. This effect is especially strong in the case of anion-additives with small radii or large charges.

2. The stability of complexes with large additives increases with increase in radius of the central ion, the stability of complexes with small additives and of amino acids decreasing with an increase in radius of the cationic complex.

3. The polarizing action of isochoric ions Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} can be characterized by means of its instability constant values for complexes of the metals enumerated with alanine (pK_1^0). Instability constant values for monotypical complexes in a series of isochoric ions are related to each other by a simple linear function.

The linear function which has been revealed can be utilized to evaluate instability constants for a series of complexes.

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COMPLEX FORMATION IN SOLUTIONS OF TERNARY SYSTEMS BY THE CRYOSCOPIC METHOD

III. $SbBr_3 - AlBr_3 - C_2H_4Br_2$ and $AlBr_3 - (C_2H_5)_2O - C_2H_4Br_2$

E. Ya. Gorenbein

Cryoscopy, as a method of physico-chemical analysis, has already been used many times. Thus, for example, Plotnikov [1] studied the interaction of dimethylpyrone with trichloroacetic acid and tribromoacetic acid in benzene by the cryoscopic method. Rabinovich [2] used this method to establish solvation. Udovenko and Usanovich [3] used this method in somewhat modified form. Lately the cryoscopic method has been extensively used by Fialkov and Muzyka [4] for the purpose of studying complex formation in solution. The principle involved is based on the fact that when interaction occurs between components of a system, depression of feeezing point should not be observed, nor should it change noticeably, but when the new component added exceeds the stoichiometnic ratio which corresponds to the new compounds formed, then this situation will be manifested by a bend in the freezing point lowering curve versus composition ($\triangle t$ vs composition). The bend in the curve corresponds to the composition of the complex formed in the solution.

The cryoscopic method of investigation, as applied by the author, differs from thermal analysis by the fact that upon cooling there should always crystallize out in solid phase only the solvent, i.e., the component whose concentration should remain constant, and the substances entering into reaction remain in the liquid phase.

It is known from the literature that the composition of the compound being formed in solution cannot always be established by any one physico-chemical method of analysis, and that several properties therefore have to be studied in order to evaluate more accurately the presence of chemical interactions and the composition of compounds forming in the liquid phase.

Proceeding from this fact, it was of interest, naturally, to apply the cryoscopic method on the one hand to such systems as those whose components produce only one compound according to the data of other methods, and on the other hand, to such systems whose components form more than one compound. Such systems are found to be the following:

$$SbBr_3 - AlBr_3 - C_2H_4Br_2 \text{ and } AlBr_3 - (C_2H_5)_2O - C_2H_4Br_2.$$

EXPERIMENTAL

Antimony bromide and aluminum bromide were synthesized and purified in the same manner as was described in the preceding articles [5]. The ethyl ester was prepared as previously [6]. The ethylene bromide was thoroughly purified and dried over fused calcium chloride, and distilled. All preparations were stored in sealed ampoules. The solutions were prepared in a special container with ground stopper and with side tube closed with glass rod by means of a rubber tube. For the $SbBr_3 - AlBr_3 - C_2H_4Br_2$ system, molten $AlBr_3$ was first introduced, followed by weighing, and then by a suspension of antimony bromide, and finally the requisite amount of solvent from a burette, controlled by weighing.

For the $AlBr_3 - (C_2H_5)_2O - C_2H_4Br_2$ system, molten $AlBr_3$ was first introduced, followed by a certain amount of solvent sufficient to dissolve the $AlBr_3$, and then about the desirable amount of ether. After weighing, calculation was made to determine what amount of solvent should be added in order to obtain the desired molecular ratio of components for the system; this amount was added from a weighing burette. Dissolution of the ether in an ethyl bromide solution of aluminum bromide was accompanied by considerable thermal effect. Measurements were carried out in a Beckman apparatus, adapted for work with hydrolyzable substances. The stirrer was nickel [7]; it was set into motion by means of an electromagnet. For the system

$$AlBr_3 - SbBr_3 - C_2H_4Br_2$$

stirring was carried out with a glass rod. For the system

$$AlBr_3 - SbBr_3 - C_2H_4Br_2$$

measurements were carried out at isomolar concentration, equal to 0.1, and for the $AlBr_3-(C_2H_5)_2O-C_2H_4Br_2$ system equal to 0.05 per mole of solvent ($C_2H_4Br_2$).

The $SbBr_3 - AlBr_3 - C_2H_4Br_2$ system

The $AlBr_3-SbBr_3$ system was investigated by melting [8], viscosity and conductivity [9] in the molten state. These investigations indicated that the compound $SbBr_3 \cdot AlBr_3$ is the electrolyte. It was of interest, naturally, to verify by the principle of isomolarity in an indifferent solvent, whether or not this compound is preserved in solution.

Aluminum bromide in ethylene bromide is associated and its degree of association does not change significantly with small change in concentration [10].

The author has investigated the change in molecular state of $SbBr_3$ in ethylene bromide upon dilution. The results are given in Table 1.

T A B L E 1
The $SbBr_3 - AlBr_3 - C_2H_4Br_2$ system
$SbBr_3$ in all experiments was 6.6237 g.

$\dfrac{M_{SbBr_3}}{M_{C_2H_4Br_2}}$	$C_2H_4Br_2$ (in g)	Freezing point lowering (Δt)	M_{SbBr_3}
0.0993	34.67	5.53	431.6
0.0893	38.55	5.09	421.1
0.0732	47.00	4.30	409.8
0.0618	55.69	3.69	403.0

As can be seen from the data of Table 1, antimony bromide in ethylene bromide solution is somewhat associated, and the degree of association changes but little with dilution. If one compares the degree of association of both components, separately, in ethylene bromide as solvent, then the $AlBr_3$ is more associated, all other factors being equal [10]. Change in degree of association of the components upon dilution need not be considerable in order to employ cryoscopic investigation of the system.

Curve 1 of Fig. 1 reflects the relationship of freezing temperature lowering to mole percent of $AlBr_3$ and $SbBr_3$ composition, the sum of which moles was taken as 100%. The greatest freezing point lowering of the solutions corresponded to the binary system

$$SbBr_3 - C_2H_4Br_2 \quad or \quad AlBr_3 - C_2H_4Br_2.$$

As this, or other components, are added under conditions of isomolar concentration, the lowering of freezing point decreases and the lowest value, Δt, corresponds to a composition of the compound formed in solution, $SbBr_3 \cdot AlBr_3$.

In addition, other properties (viscosity, electroconductivity) which were studied by the author, together with Smolentsev [11], for the same system, except at another isomolar concentration equal to 0.4 per mole of ethylene bromide, are compared,

It can be seen on the curves of Fig. 1 that the maxima for corrected κ' (Curve 4) and specific electroconductivity,κ (Curve 2) uncorrected for viscosity,as well as viscosity, η, (Curve 3), and the maximum depression, Δt, (Curve 1), correspond to an equimolecular composition for the compound forming in solution.

The results obtained indicate without doubt that the electrolyte in this solution, independent of isomolar concentration of 0.1 or 0.4, is found to be the $SbBr_3 \cdot AlBr_3$ complex.

The molecular weight of this complex, proceeding from the depression, corresponding to an equimolecular composition of components $AlBr_3$ and $SbBr_3$, is equal to 453.5, i.e., is smaller than that calculated according to the formula, which indicates instability of the compound at this concentration of solution.

On the whole, the minimum for molecular electroconductivity in solutions with low D_p, correspond as a rule to a monomolecular state of the electrolyte.
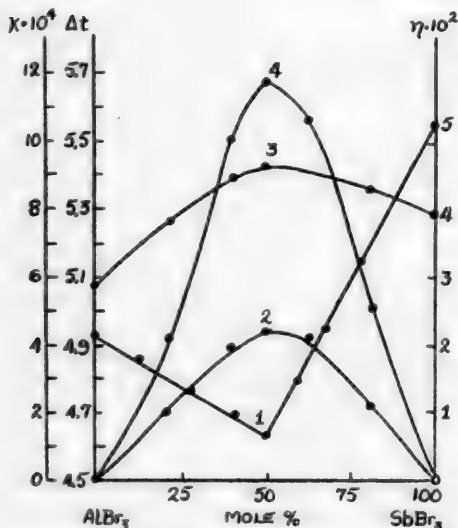

Fig. 1. Relation of freezing point lowering to $AlBr_3$ and $SbBr_3$ content (Curve 1),specific electroconductivity (Curve 2), viscosity Curve 3), and electroconductivity, corrected for viscosity, of the $SbBr_3 - AlBr_3 - C_2H_4Br_2$ system (Curve 4).

For calculation of the instability constant of a complex, several determinations of Δt should be carried out at isomolecular concentration, in which case the electroconductivity can be ignored, and the apparent molecular weight will be lower than that corresponding to the formula $SbBr_3 \cdot AlBr_3$. The instability constant in the given case is expressed by an equation, which is analogous to the thermal dissociation constant

$$SbBr_3 \cdot AlBr_3 \rightleftharpoons SbBr_3 + AlBr_3; \quad K = \frac{a^2 \cdot C}{1-a} \ .$$

The degree of decomposition is determined by the expressions $\left(\dfrac{\Delta t'}{\Delta t} - 1 \right)$, where $\Delta t'$ = lowering of the freezing point of the solution, determined experimentally; Δt = theoretically calculated freezing temperature of the solution, under conditions in which the complex is not dissociated, under the author's conditions the constant being equal to 0.01238, $a = 0.389$. This provides the opportunity for evaluating the degree of stability of the complex under the given conditions.

The $AlBr_3 - (C_2H_5)_2O - C_2H_4Br_2$ system

Aluminum halide ethers as electrolytes have frequently attracted the attention of investigators [12]. Up to the present time, however, it has not been determined whether $AlBr_3$ forms only one complex compound with $(C_2H_5)_2O$, or more. According to the thermal analysis data, the presence of one compound $AlBr_3 \cdot (C_2H_5)_2O$ has been established, but the system has not been studied over the entire range of concentrations [13].

The investigational procedure used by the author for interaction between two substances in a third indifferent solvent provides an opportunity for observing changes of one or more properties over the entire range of concentrations of the $AlBr_3$ and $(C_2H_5)_2O$ components.

The given system was investigated by the authors through conductivity and by the cryoscopic method. The results of electroconductivity measurements are compiled in Table 2; cryoscopic data are presented graphically.

TABLE 2

Mole ratio $\dfrac{AlBr_3 + (C_2H_5)_2O}{C_2H_4Br_2} = 0.05$ Temperature 20°

$AlBr_3$ (in mole %)	$\kappa \cdot 10^5$	$AlBr_3$ (in mole %)	$\kappa \cdot 10^5$	$AlBr_3$ (in mole %)	$\kappa \cdot 10^5$
0	-	48.76	3.12	71.60	0.29
21.35	0.82	50.75	1.09	79.10	0.26
26.09	1.04	52.58	0.20	100	-
38.04	2.32	62.66	0.38	-	-
41.78	2.41	69.49	0.37	-	-

It follows from the electroconductivity data that aluminum bromide forms two compounds with ether, of the compositions $AlBr_3 \cdot (C_2H_5)_2O$ and $2AlBr_3 \cdot (C_2H_5)_2O$. The sharp decrease in electroconductivity after reaching a maximum is evidently affected by a shifting of the equilibrium to the side of formation of the $2AlBr_3 \cdot (C_2H_5)_2O$ complex, which is a poor conductor of the electric current.

As can be seen from Fig. 2, for this sytem, as well as for the preceding, the slightest decrease in freezing temperature corresponds to equimolecular composition of $AlBr_3 \cdot (C_2H_5)_2O$ compound. Consequently, the cryoscopic method brings to light quite readily one compound of the liquid phase. A certain scattering of the points is apparently caused by volatility of the ether.

It should be mentioned that the color of the solution changes upon transition from the predominating concentration of $AlBr_3$ to a predominating concentration of ether, from light yellow to colorless.

EVALUATION OF RESULTS

Upon investigating the electroconductivity of ternary systems under conditions of constant ratio of two components and variable concentration of the third, quite frequently the conductivity maxima do not correspond to the composition of the compound forming in the solution. Thus, for example, on the basis of an electroconductivity maximum for the system $SbBr_3 - AlBr_3 - C_6H_6$, a conclusion was made that in the solution a compound of the composition $SbBr_3 \cdot Al_2Br_6$ [14] is formed.
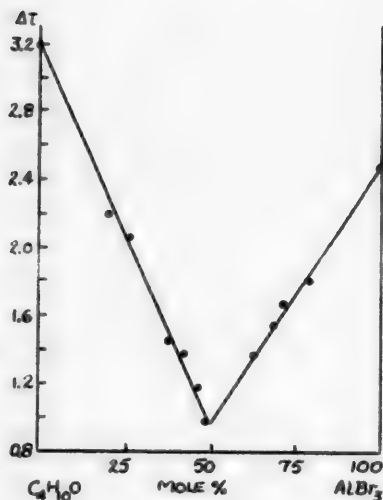
Fig. 2. Relation of freezing point lowering to composition for the $AlBr_2 - (C_2H_5)_2O - C_2H_4Br_2$ system.

$$\frac{M_{AlBr_3} + M_{C_4H_{10}O}}{M_{C_2H_4Br_2}} = 0.05.$$

The author has demonstrated that the maximum disappears if viscosity is taken into account [11]. It should be mentioned that the composition of the compound in the concentrated solution can be determined, usually, by taking viscosity into account. The method used by the authors provides an opportunity for investigating any change in property over the entire concentration range for two components, with constant concentration of the third component, the indifferent solvent, and for working with small amounts of substances.

The advantage of this method lies in the fact that interaction of the substances with limited solubility at low temperature can be investigated, which in turn provides an opportunity for avoiding thermal decomposition. This method, however, is not without shortcomings. The principal disadvantage is that the third component (solvent) must be indifferent with respect to the other two components, which is not always easy to select. Investigation of lowering in the freezing point of solutions, in contrast to other properties (electroconductivity, viscosity, surface tension, and others) differs also in the fact that the applicability of the method is conditioned by concentration of the components. The cryoscopic method is applicable to solutions of such concentration that, upon crystallization, only solvent separates in the solid phase. Comparison of data on various properties for the $SbBr_3 - AlBr_3 - C_2H_4Br_2$ system, studied at isomolar concentrations of 0.1 and 0.4, has indicated that the complex $SbBr_3 \cdot AlBr_3$ is the electrolyte in the given system. But the system $AlBr_3 - (C_2H_5)_2O - C_2H_4Br_2$ which was investigated indicated that, according to conductivity, two compounds, $AlBr_3 \cdot (C_2H_5)_2O$ and $2AlBr_3 \cdot (C_2H_5)_2O$, are formed in the system, and according to cryoscopic data that only one compound $AlBr_3 \cdot (C_2H_5)_2O$ is formed. This fact, however, does not enable us to claim that the cryoscopic method provides an opportunity for detecting in the liquid phase only one compound.

SUMMARY

1. The interaction of $AlBr_3$ with $SbBr_3$ in ethylene bromide as solvent has been studied by the cryoscopic method, and $AlBr_3$ with $(C_2H_5)_2O$ in the same solvent, by the cryoscopic method and by electroconductivity over the entire range of concentration.

2. It has been established that in the $SbBr_3 - AlBr_3 - C_2H_4Br_2$ system, the $SbBr_3 \cdot AlBr_3$ complex is the electrolyte. The instability constant has been calculated for the compound from cryoscopic data.

3. Two compounds, $AlBr_3 \cdot (C_2H_5)_2O$ and $2AlBr_3 \cdot (C_2H_5)_2O$, are formed in the system $AlBr_3 - (C_2H_5)_2O - C_2H_4Br_2$, according to electroconductivity data, and one compound, $AlBr_3 \cdot (C_2H_5)_2O$, according to cryoscopic data.

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INTERRELATIONSHIPS OF LITHIUM, SODIUM AND POTASSIUM SULFATES IN MELTS

THE TERNARY SYSTEM OF LITHIUM, SODIUM AND POTASSIUM SULFATES

E. K. Akopov and A. G. Bergman

In the D. I. Mendeleev system, in the first four groups, the first representative of the main group (2nd horizontal series) displays properties transitional to the element of the next group in the 3rd row, and it is only the second or third representative which fully reveals the characteristic properties of its group.

Lithium, being the leading element of the first main subgroup of the periodic system, occupies a special position with respect to the other alkali metals. This peculiarity consists in the fact that in its properties lithium salts in many ways resemble compounds of the alkaline earth metals, and magnesium above all. For example, lithium and magnesium salts do not give a compound with the common anion; they crystallize from melts either in the form of a continuous series of solid solutions, or they represent systems with a simple eutectic. This characteristic of lithium, distinct from its analogs — the alkali metals — is revealed by the fact that its salts have a tendency to form compounds with salts of the other alkali metals. Among the lithium salts, its sulfate has a clear-cut ability to form complexes with sulfates of the alkali metals.

Investigations by the authors have demonstrated that lithium, sodium and potassium sulfates, though among the simplest of inorganic salts, display extremely complex chemical interrelationships in melts: they form among themselves complex compounds of the double salt type, as well as ternary salts.

The interrelationships of lithium, sodium and potassium sulfates have been investigated for the first time by the present authors, in the form of a ternary system, on the basis of a prism of the composition of a reciprocal quaternary system composed of the chlorides and sulfates of lithium, sodium and potassium, ...

EXPERIMENTAL

Investigation was carried out in a platinum crucible with platinum stirrer, by the visual polythermal method. Temperature of appearance of the first cyrstals was measured by means of a Pt-Rh—Au-Pd-Pt thermocouple, 0.5 mm in diameter, and a millivoltmeter.

The initial chemically pure salts were recrystallized twice. The melting points adopted for lithium, sodium and potassium sulfates were, respectively, 856, 884 and 1069°. All compositions are expressed in molecular percentage.

Investigation of the given sytem was attended with great difficulties. Since the sulfates of the given elements crystallize poorly from melts, and in several areas of the system there occurs glass formation and gelling, and since supercooling frequently took place, determination of the start of rystallization presented formidable difficulties. As indicated from the authors' experiments deviation in the melting poirt of the composition at cross-sectional points of the internal part fluctuated within the range of 1%, which satisfies the requirements pertaining to accuracy of determination.

Binary Systems

1. $Li_2SO_4 - Na_2SO_4$ was investigated by R. Nacken [1] through the use of heating and cooling curves, followed by other investigators using the thermographic method, and also the visual polythermal method, the latter method being used by the present authors.

The authors' data for the liquidus curve deviate considerably from the data of R. Nacken. According to the authors' data, lithium and sodium sulfates form two compounds melting with decomposition, of the composition 1:1

$Li_2SO_4 \cdot Na_2SO_4$ and $1 : 2 (Li_2SO_4 \cdot 2Na_2SO_4)$.

In Fig. 1 (according to the data of Table 1), the liquidus diagram for $Li_2SO_4-NaSO_4$ is given. It consists of four crystallization branches: Na_2SO_4 compounds $1 : 1$, $1 : 2$ and a -Li_2SO_4, which intersect at 637° and 62.5 % Na_2SO_4, at 620° and 48% Na_2SO_4, and at 596° and 36.5% Na_2SO_4, respectively.

2. $Li_2SO_4-K_2SO_4$ was investigated by R. Nacken [1] and other investigations, the present authors included.

Lithium and potassium sulfates form a stable compound of the composition $1 : 1$, with a melting point of 732°. The authors have also established formation of a second compound, melting with decomposition, of the composition $2 : 1 (2Li_2SO_4 \cdot K_2SO_4)$ with m.p. 550°; it can be called "lithium langbeinite".

The liquidus diagram for the system $Li_2SO_4-K_2SO_4$ (Fig. 1) consists of five branches: $a/\beta = Li_2SO_4$, compounds $2 : 1$, $1 : 1$, and K_2SO_4.

The heteromorphic transformation point of Li_2SO_4 is at 572° and 83% Li_2SO_4. Eutectic points at 532° and 81% Li_2SO_4, and at 712° and 39.5% Li_2SO_4; transitional point at 550° and 76.5% Li_2SO_4, maximum at 732° and 50% Li_2SO_4.
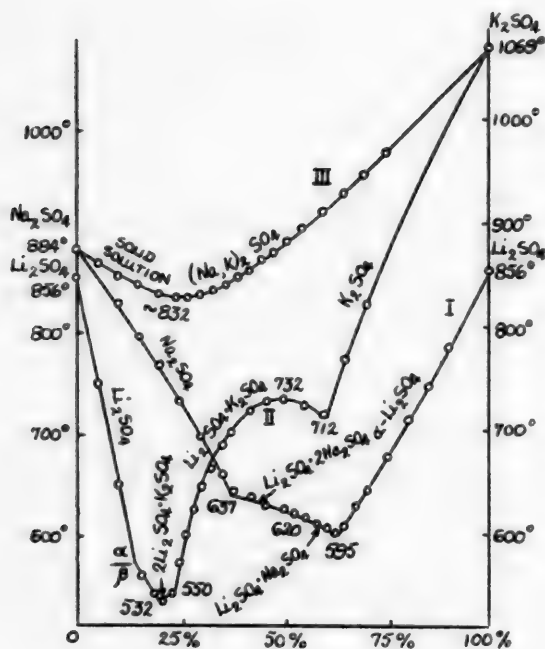
Fig. 1. Auxiliary binary systems of the ternary system, Li, Na, K‖SO_4.
I = Lithium and sodium sulfates;
II = lithium and potassium sulfates;
III = sodium and potassium sulfates;

$Na_2SO_4-K_2SO_4$ was investigated by Nacken [1], Janecke [2], and the present authors. Sodium and potassium sulfate form a continuous series of solid solutions, with a minimum, according to Nacken, at 830° and 20 % K_2SO_4, and according to Janecke, 845° and 23.5% K_2SO_4, and according to the authors's data, at 832° and 25% K_2SO_4. According to the data of the first two authors, solid solutions below the liquidus line decompose, and the components convert into another crystalline modification (rhomboidal), Na_2SO_4 at 232° and K_2SO_4 at 590° according to Nacken, and 225 and 587°, respectively, according to Janecke. Moreover, at 476° the solid solutions decompose with formation of a compound of the composition $1 : 1$, which forms organic solid solutions with its components.

In Fig. 1 (according to the data of Table 1) a diagram for melting of the system $Na_2SO_4-K_2SO_4$, according to the authors' data, is given.

Internal Sections

20 internal sections were studied (Figs. 2,3 and 4, Tables 2,3,4,5); the general characteristics for these profiles are given in Table 6.

TABLE 1
Binary Systems

Li_2SO_4–Na_2SO_4				Li_2SO_4–K_2SO_4				Na_2SO_4–K_2SO_4			
Li_2SO_4 (in %)	Temperature	Li_2SO_4 (in %)	Temperature	K_2SO_4 (in %)	Temperature	K_2SO_4 (in %)	Temperature	K_2SO_4 (in %)	Temperature	K_2SO_4 (in %)	Temperature
0	884°	55	616°	0	856°	32	666°	0	884°	42	858°
10	828	58	611	5	750	35	688	5	870	45	868
15	796	60	608	10	650	32	702	10	856	48	876
20	768	62	604	15	556	42	722	15	848	51	886
25	700	64	608	18	542	46	730	20	836	55	900
30	696	67	628	20	536	50	732	24	833	60	915
35	660	70	644	22	542	55	726	27	832	65	932
38	644	75	676	24	574	60	716	30	836	70	950
42	636	80	712	26	600	65	770	33	841	75	970
45	628	85	744	28	625	70	825	36	846	100	1069
50	626	90	782	30	648	100	1069	39	852	-	-
52	620	100	856	-	-	-	-	-	-	-	-

TABLE 2
A – Li_2SO_4 (in %)

Section I				Section II				Section VI			
A	Temperature	A	Temperature	A	Temperature	A	Temperature	A	Temperature	A	Temperature
0	846°	42	624°	0	834°	34	644°	0	912°	30	700°
5	812	46	616	5	798	36	636	5	876	34	686
10	786	50	606	10	770	38	628	10	842	38	667
15	750	54	600	15	742	40	624	12	820	42	673
20	724	58	596	18	722	42	614	15	796	46	670
25	690	62	590	22	690	45	611	18	770	50	660
30	660	66	580	25	674	48	608	21	748	52	654
34	640	70	578	30	654	50	606	24	732	55	640
38	632	75	625					27	718	58	632

A full projection is given in Fig. 5 for the melting diagram of Li, Na, K ‖ SO_4 system on on a composition triangle, where the isotherms are drawn at every 50°, and one at 25° (indicated by the broken line).

Of special interest are the internal phases, symbolized by the letters [A] and [B]. This section of the diagram was investigated in more detail by the authors; although the crystallization fields for phases [A] and [B] pass through 14 internal sections (Fig. 4), their crystallization branches are clearly defined on the curves.

In addition, the authors investigated four internal sections through the quaternary reciprocal prism system of Li, Na, K‖Cl, SO_4 composition, whose diagrams completely confirmed the reality of the [A] and [B] phases.

Lithium sulfate is found to be a good complex former in melts: with sodium and potassium sulfates it forms two compounds, respectively. It is quite understandable that these sulfates also form compounds inside the system. Sodium and potassium sulfates give a compound of the composition 1 : 1, but the maximum temperature for its existence is lower than the formation temperature of the internal phases [A] and [B] Moreover, in the reciprocal system Na, K‖Cl, SO_4 ivesstigated by the authors, solid solutions below 706° decompose with formation of an independent phase [X]; but the configuration for the prism of phase [X] composition does not border on the [A] phase, and it should therefore be

assumed that they are ternary complex compounds, highly dissociated, and possibly forming solid solutions with the components.
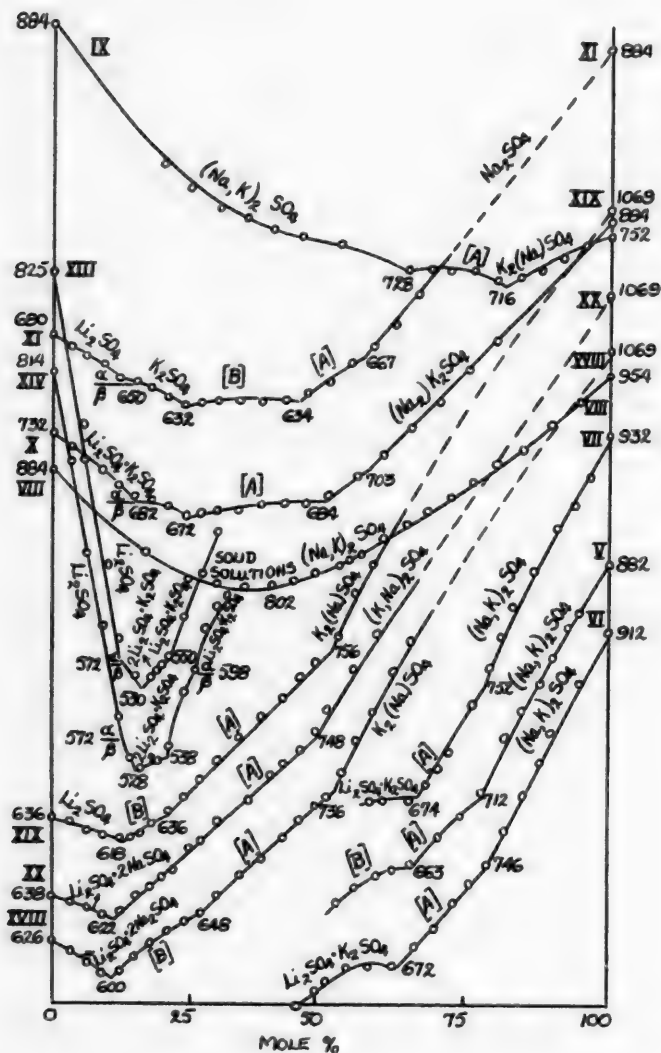
Fig. 2. Internal sections of Li, Na, K∥SO₄ system
[A] and [B] - internal phases of the system, obscure in composition

A projection of the crystallization pattern on the side of $Na_2SO_4 - K_2SO_4$ is given in Fig. 6, by means of which the monovariant crystallization curves are located, as well as the non-variant ternary points, among which 1 is eutectic and 9 are transitional.

Triangulation of the system, however (Fig. 7) is complicated since the accurate compositions for the internal phases [A] and [B] (compounds) are not known; they were arbitrarily selected by the authors.

The sides of the phase triangles are indicated by the continuous lines, which were obtained on the basis of known compositions for the compound on the side; the broken lines of the phase triangle result from triangulation

on the basis of internal compounds, whose compositions are taken tentatively. Arrows indicate position of the non-variant point for the correspondnig phase triangles.

T A B L E   3
A - Li$_2$SO$_4$, B - K$_2$SO$_4$ (in %)

Cross section V		Cross section VII		Cross section XIII		Cross section XIV		Cross section XVII	
A	Temp.	A	Temp.	B	Temp.	B	Temp.	B	Temp.
-	882°	-	932°	-	825°	-	814°	-	616°
5	846	3	902	5	714	3	752	3	602
10	814	6	884	10	618	6	686	6	596
12	796	9	866	12	564	9	634	9	590
15	776	13	836	15	588	12	568	15	596
18	758	16	810	18	536	14	538	21	619
22	718	18	788	19	542	16	530	24	630
26	700	21	766	20	547	18	535	27	640
30	826	24	740	21	550	21	546	-	-
35	662	28	705	22	555	24	586	-	-
38	662	30	694	24	580	26	602	-	-
41	657	32	680	27	640	28	632	-	-
45	648	35	673	30	660	30	648	-	-
48	636	40	670	-	-	32	658	-	-
-	-	42	672	-	-	-	-	-	-

T A B L E   4
A - Li$_2$SO$_4$, B - K$_2$SO$_4$, C - Na$_2$SO$_4$ (in %)

Cross section III		Cross section IV		Cross Section X		Cross section XV		Cross section XVII		Cross section XX	
A	Temp.	A	Temp.	C	Temp.	B	Temp.	B	Temp.	B	Temp.
0	834°	0	858°	0	732°	0	782°	0	626°	0	638°
5	802	3	842	3	723	2	720	3	618	3	634
10	776	6	818	6	712	4	670	6	612	6	630
14	754	9	798	9	705	6	630	9	604	9	625
18	730	12	782	12	696	9	564	12	603	12	628
20	718	15	756	15	688	12	514	15	615	15	638
24	692	18	740	18	685	14	522	18	624	18	647
26	682	21	720	21	680	16	532	21	632	20	653
28	670	24	698	24	674	18	540	24	640	22	658
32	654	27	680	27	674	20	540	27	648	25	674
34	644	30	672	30	676	22	550	30	660	28	678
36	634	33	660	34	678	24	566	34	674	30	694
38	630	36	648	38	680	26	584	38	686	36	708
42	620	38	648	42	682	28	620	42	702	40	728
45	614	40	646	46	684	30	634	45	715	42	735
48	605	42	644	50	688	32	634	48	726	45	746
51	597	45	637	55	702	34	674	50	732	48	760
55	588	48	627	60	716	39	692	52	750	50	775
58	584	52	615	65	735	42	700	55	774	52	780
62	576	56	590	70	754	45	708	58	794	55	805
65	570	60	578	75	778	50	712	62	824	58	831
68	564	64	574	80	798	55	704	65	846	62	852
72	558	68	566	100	884	60	716				
75	550					63	740				
77	578										

TABLE 5

B - K$_2$SO$_4$, C - Na$_2$SO$_4$ (in %)

Cross section VIII		Cross section IX		Cross section XI		Cross section XII		Cross section XVI		Cross section XIX	
C	Temp.	C	Temp.	C	Temp.	C	Temp.	B	Temp.	B	Temp.
0	954°	0	752°	0	680°	0	560°	0	748°	0	636°
10	918	5	746	3	673	3	542	3	624	3	632
15	902	10	736	6	666	6	525	8	549	6	626
20	890	15	728	9	660	9	538	15	556	9	622
24	876	20	717	12	651	12	548	16	558	12	620
28	866	24	721	15	648	15	552	18	562	14	620
32	856	26	728	18	645	18	560	21	568	16	624
36	848	28	728	21	638	21	567	24	600	18	630
40	836	32	730	24	631	25	575	26	615	21	640
44	824	36	728	27	634	30	586	28	632	24	650
46	822	40	736	30	634	34	594	30	646	27	662
48	818	48	746	34	635	38	602	32	656	30	678
52	818	55	752	38	634	42	608	35	670	34	694
56	808	60	757	42	635	46	616	38	678	38	708
60	804	65	766	46	639	50	626	42	680	42	722
65	802	70	774	50	648	52	628	45	696	45	738
75	806	75	788	54	662	55	632	50	698	48	748
83	826	80	804	58	674	58	636	55	694	52	778
100	884	100	884	62	690	62	660	58	716	55	798
-	-	-	-	66	712	66	683	62	764	58	818
-	-	-	-	-	-	70	708	-	-	-	-
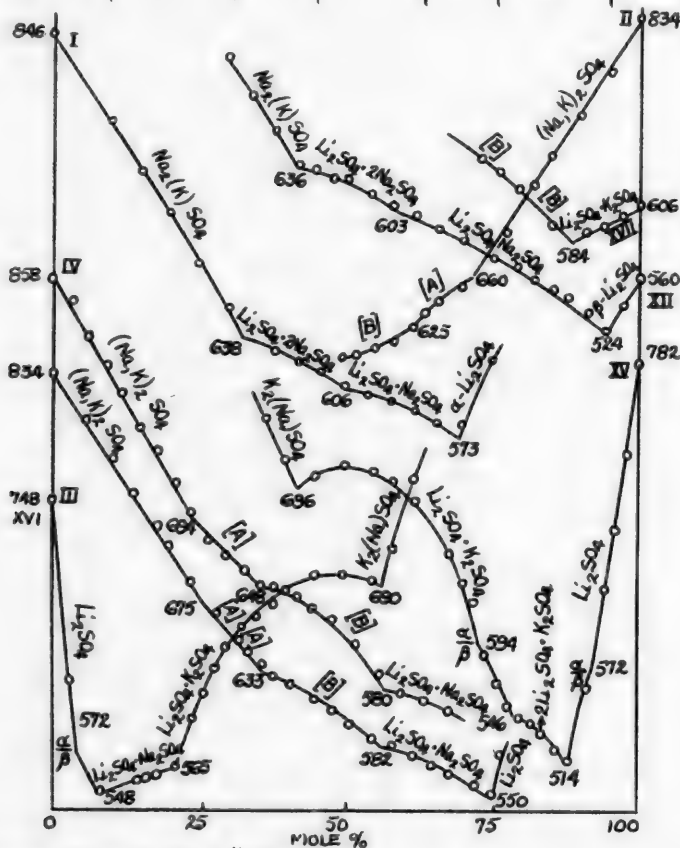
Fig. 3. Internal sections of the Li, Na, K ‖ SO$_4$ system.

[A] and [B] = internal sections of the phase with obscure composition.

TABLE 6

$(Na, K)_2SO_4$ — continuous series of solid solutions of sodium and potassium sulfates $Na_2(K)SO_4$ and $K_2(Na)SO_4$ — sulfates of the same elements resulting from decomposition of the solid solutions. $D = Li_2SO_4 \cdot K_2SO_4$; $G = 2Li_2SO_4 \cdot K_2SO_4$; $D_1 = Li_2SO_4 \cdot Na_2SO_4$; $D_2 = Li_2SO_4 \cdot 2Na_2SO_4$

Section number	Initial mixture of components (in %)	Component added	I	Crossection I (in %)*	Temperature	II	Crossection II (in %)*	Temperature	III	Crossection III (in %)*	Temperature	IV	Crossection IV (in %)*	Temperature	V
I	$15K_2SO_4+85Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	32.5	638°	D_2	50.5	606°	D_1	62.5	573°	a-Li_2SO_4	75.0	550°	Li_2SO_4
II	$22K_2SO_4+78Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	28.0	660	[A]	38.0	625	[C]	56.5	582	D_1			
III	$30K_2SO_4+70Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	25.5	675	[A]	36.0	633	[C]	57.0	580	D_1			
IV	$42K_2SO_4+58Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	25.0	694	[A]	36.5	648	[C]						
V	$50K_2SO_4+50Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	23.0	712	[A]	35.5	663	[C]	57.0	580	D_1			
VI	$59K_2SO_4+41Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	21.5	746	[A]	36.5	672	β-D						
VII	$65K_2SO_4+35Na_2SO_4$	Li_2SO_4	$(Na, K)_2SO_4$	22.0	752	β-D	33.5	674	β-D						
VIII	$85K_2SO_4+15Li_2SO_4$	Na_2SO_4	$K_2(Na)SO_4$	18.5	716	[A]	35.0	728	$(Na, K)_2SO_4$	49.0	684	$Na_2(K)SO_4$	56.0	703	$(Na, K)_2SO_4$
IX	$65K_2SO_4+35Li_2SO_4$	Na_2SO_4	$K_2(Na)SO_4$	16.0	682	[A]	25.5	672	[A]	45.0	634	[A]	56.0	663	$(Na, K)_2SO_4$
X	$50K_2SO_4+50Li_2SO_4$	Na_2SO_4	a-D	13.0	650	β-D	24.0	632	[C]	59.0	636	$Na_2(K)SO_4$			
XI	$35K_2SO_4+65Li_2SO_4$	Na_2SO_4	a-D	6.0	524	β-D	41.0	603	D_2			D_1			D_1
XII	$15K_2SO_4+85Li_2SO_4$	Na_2SO_4	β-Li_2SO_4	12.5	572	D_1	16.5	530	D_2						
XIII	$3Na_2SO_4+97Li_2SO_4$	K_2SO_4	a-Li_2SO_4	12.5	572	β-Li_2SO_4	15.0	528	G	28.5	550	a-D	25.5	598	a-D
XIV	$5Na_2SO_4+95Li_2SO_4$	K_2SO_4	a-Li_2SO_4	8.0	572	β-Li_2SO_4	12.0	514	G	21.0	538	β-D	26.5	594	a-D
XV	$10Na_2SO_4+90Li_2SO_4$	K_2SO_4	a-Li_2SO_4	4.0	572	β-Li_2SO_4	8.0	548	G	21.0	546	β-D	56.5	690	$K_2(Na)SO_4$
XVI	$20Na_2SO_4+80Li_2SO_4$	K_2SO_4	a-Li_2SO_4		572	β-Li_2SO_4			G_1	21.5	565	β-D			
XVII	$40Na_2SO_4+60Li_2SO_4$	K_2SO_4	D_1	11.5	584	[C]	27.0	648	[A]	49.0	684				
XVIII	$50Na_2SO_4+50Li_2SO_4$	K_2SO_4	D_2	11.0	600	[C]	20.5	636	[A]	51.0	736	$K_2(Na)SO_4$			
XIX	$55Na_2SO_4+45Li_2SO_4$	K_2SO_4	D_2	11.5	618	[C]			[A]	50.5	756	$K_2(Na)SO_4$			
XX	$60Na_2SO_4+40Li_2SO_4$	K_2SO_4	D_2	11.0	622	[A]	46.5	748	$K_2(Na)SO_4$			$K_2(Na)SO_4$			

(Branches of the crystallization curves and their cross sections)

Note (section VIII): Solid p—p $(Na,K)_2SO_4$, minimum at 802

* Percent of added component.

1505

TABLE 7

No.	Name of the phase triangle	Ternary point	Temp- erature	Composition of ternary point (in mole%)		
				Li_2SO_4	Na_2SO_4	K_2SO_4
1	$2Li_2SO_4 \cdot K_2SO_4 - Li_2SO_4 - Li_2SO_4 \cdot Na_2SO_4$	E	512°	79.0	9.	12
2	$2Li_2SO_4 \cdot K_2SO_4 - Li_2SO_4 \cdot K_2SO_4 - Na_2SO_4$	P_1	536	73.0	6.5	20.5
3	$Li_2SO_4 \cdot K_2SO_4 - [B] - Li_2SO_4 \cdot Na_2SO_4$	P_2	568	58.0	19.25	22.75
4	$Li_2SO_4 \cdot Na_2SO_4 - [B] - Li_2SO_4 \cdot 2Na_2SO_4$	P_3	586	48.0	41.5	10.5
5	$[A] - [B] - Li_2SO_4 \cdot 2Na_2SO_4$	P_4	620	38.0	50.5	11.5
6	$[A] - Li_2SO_4 \cdot 2Na_2SO_4 - Na_2SO_4$	P_5	633	29.0	62.0	9.0
7	$[A] - (2Na_2SO_4 \cdot K_2SO_4) - Na_2SO_4$	P_6	668	25.0	56.0	19.0
8	$Li_2SO_4 \cdot K_2SO_4 - [A] - [B]$	P_7	667	38.0	25.5	36.5
9	$[A] - (2Na_2SO_4 \cdot K_2SO_4) - K_2SO_4$	P_8	756	34.0	10.5	55.5
10	$Li_2SO_4 \cdot K_2SO_4 - [A] - K_2SO_4$	P_9	682	20.5	29.5	50.0

* E , ternary eutectic point, P, ternary transitional point
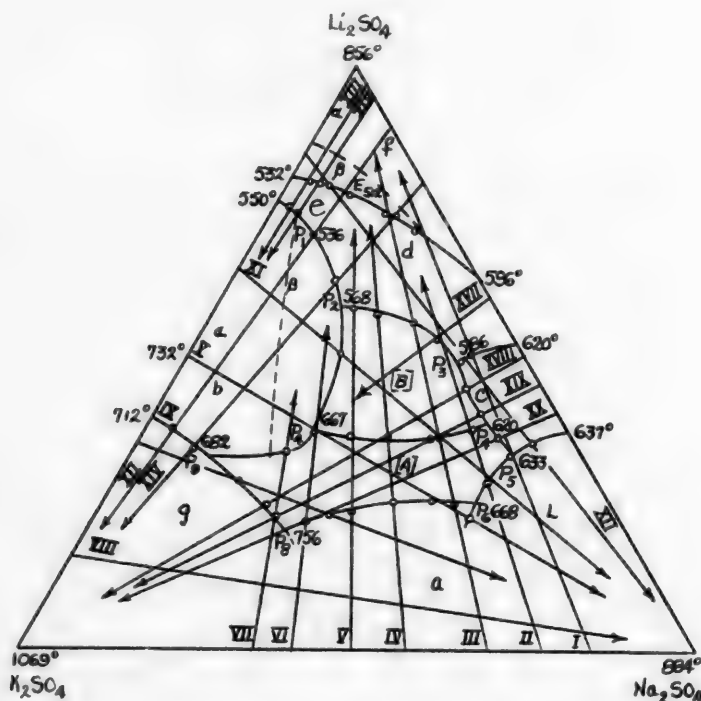
Fig. 4. Scheme of arrangement of internal sections for the system Li, Na, K ‖ SO₄.
a) solid solutions $(Na,K)_2SO_4$, b) $Li_2SO_4 \cdot K_2SO_4$, c) $Li_2SO_4 \cdot 2Na_2SO_4$, d) $Li_2SO_4 \cdot Na_2SO_4$, e) $2Li_2SO_4 \cdot K_2SO_4$, f) a/β -Li_2SO_4, g) $K_2(Na)SO_4$ h) $Na_2(K)SO_4$.

It can be seen in Fig. 7 that the primary triangle of Li, Na, K ‖ SO₄ system is broken up into 10 phase (secondary) triangles, which are given in Table 7.

The diagram for crystallization surface of the system consists of 10 areas, among which two correspond to hetero- morphic modifications in Li_2SO_4 with a transition point at 572° and two homomorphic modifications for the compound $Li_2SO_4 \cdot K_2SO_4$, whose transition between themselves in the given system occurs within the interval of 555-670° (accord- ing to the branched projection, Fig. 6). The area occupied by each field in relation to the area of the triangle of com- positions, is given in Table 8.

It should be indicated that the courses of the isotherms differ noticeably from one another in the internal planes. In the crystallization field of solid solutions $(Na, K)_2SO_4$, the isotherms 750-800° are characterized by considerable

concavity toward $Na_2SO_4-K_2SO_4$. Moreover, in this area two monovariant curves radiate out from the two ternary points (p_6 and p_8), indicated by the broken line.

Fig. 5. Projection of the melting diagram for the ternary system Li, Na, K $\|SO_4$ in the composition triangle.
a) solid solutions $(Na,K)_2SO_4$ b) $Li_2SO_4 \cdot K_2SO_4$, c) $Li_2SO_4 \cdot 2Na_2SO_4$, d) $Li_2SO_4 \cdot Na_2SO_4$, e) $2Li_2SO_4 \cdot K_2SO_4$,
f) a/β -Li_2SO_4, g) $K_2(Na)SO_4$, h) $Na_2(K)SO_4$. [A] and [B] = internal phases of obscure composition

Fig. 6. Projection of the ternary system at one side of the triangle $Na_2SO_4-K_2SO_4$.

[A] and [B] = internal phases of obscure composition.
The other symbols same as in Fig. 5.
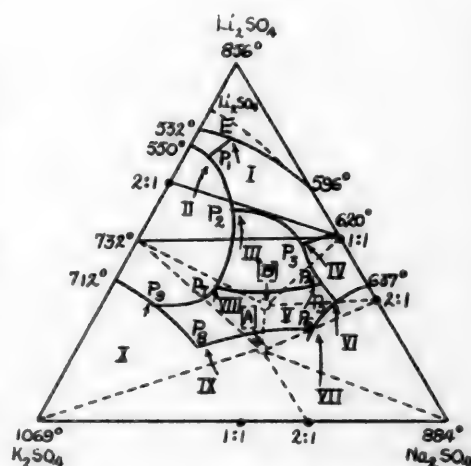
Fig. 7. Triangulation scheme for the ternary system.
Explanation in text of Table 7.

TABLE 8

Field no.	Name of area of crystallization	Contained (%)	Field no.	Name of area of crystallization	Contained (%)
1	Solid solution $(Na,K)_2SO_4$	50.10	6	β -Li_2SO_4	1.30
2	α -$Li_2SO_4 \cdot K_2SO_4$	8.84	7	α -Li_2SO_4	4.36
3	β -$Li_2SO_4 \cdot K_2SO_4$	6.34	8	Phase [A]	8.85
4	$Li_2SO_4 \cdot Na_2SO_4$	8.17	9	Phase [B]	7.70
5	$Li_2SO_4 \cdot 2Na_2SO_4$	3.31	10	$2Li_2SO_4 \cdot K_2SO_4$	1.03

SUMMARY

1. The ternary system, Li, Na, K $\parallel$ SO_4 has been investigated by the melting point method.

2. In the system two internal phases, ternary complexes, have been established.

3. In the system are present one ternary eutectic at 512°, of the composition 12% K_2SO_4, 9% Na_2SO_4 and 79% Li_2SO_4, and 9 triple transitional points.

4. Triangulation of the system has been carried out with 10 phase triangles.

5. Diagrams for the system consist of 10 crystallization areas; the largest area occupies the field of solid solution $(Na, K)_2SO_4$, in which are plotted monovariant curves of rupture for the solid solutions.

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REVERSIBLE-ADIAGONAL SYSTEM OF SODIUM AND POTASSIUM-CHLORIDES AND SULFATES

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At the base of the given system is the exchange reaction $K_2Cl_2 + Na_2SO_4 \rightleftharpoons Na_2Cl_2 + K_2SO_4$.

The conditional thermal effect of the exchange reaction amounts to 0.38 kcal per 1 gram equiv. toward the side $Na_2Cl_2 + K_2SO_4$.

Jänecke [1] investigated this system earlier. The two different binary systems $Na_2Cl_2-K_2Cl_2$ and $Na_2SO_4-K_2SO_4$ represent continuous series of solid solutions with minima, and the other two different systems are found to be eutectic. The diagram for crystallization points is composed, according to Jänecke, of two areas of sodium and potassium sulfates and chlorides solid solutions, which divide the combined crystallization curves at a minimum of 518°.

The system has been investigated in detail by the authors. It was found that the crystallization diagram for a given interrelated system is more complicated.

The above-indicated solid solutions decompose within the system, and the decomposition products of the sulfates form a phase below 706°, to which, for purposes of orientation, the composition 3 : 1 ($3NaSO_4 \cdot K_2SO_4$) or 2 : 1 ($2Na_2SO_4 \cdot K_2SO_4$) has been attributed.

EXPERIMENTAL

Investigation was carried out by the visual-polythermal method [2,3]. The initial salts, chemically pure, were recrystallized twice; the melting temperatures for sodium and potassium sulfates were adopted, respectively, as 884 and 1069°, and the chlorides as 800 and 774°.

In the work, only a portion of the investigated cross-sections and experimental points are given. All compositions are expressed as molecular percentage.

TABLE 1

$Na_2Cl_2-K_2Cl_2$		$K_2Cl_2-K_2SO_4$				$Na_2SO_4-K_2SO_4$				$Na_2Cl_2-Na_2SO_4$	
Na_2Cl_2 (in %)	Temperature	K_2Cl_2 (in %)	Temperature	K_2Cl_2 (in %)	Temperature	K_2SO_4 (in %)	Temperature	K_2SO_4 (in %)	Temperature	Na_2Cl_2 (in %)	Temperature
0	774°	0	1069°	57.5	692°	0	884°	42	858°	0	884°
15	760	6	1026	62.0	698	5	870	45	869	20.4	724
30	697	12	986	66.0	706	10	856	48	876	25.5	691
50	660	18	948	69.5	713	15	848	51	886	30.8	661
60	665	24.5	902	70.0	724	20	836	55	900	35.0	628
75	700	30.5	866	77.0	734	24	833	60	915	48.0	679
75	700	30.5	866	77.0	734	24	833	60	915	48.0	679
100	800	36.5	828	81.0	740	27	832	65	932	61.0	716
		42.5	790	85.0	750	30	836	70	950	71.3	748
		48.5	754	89.0	760	33	841	75	970	81.3	762
		51.5	732	94.5	770	36	846	100	1069	91.3	785
		54.5	713	100.0	774	39	852			100.0	800

Binary Systems. The liquidus curves for binary systems are shown in Fig. 1 (Table 1). 1. $Na_2Cl_2-K_2Cl_2$ — a continuous series of solid solutions with minimum at 658° and 50% of components; at lower temperature, the solid solutions decomposed below 500° (Figs. 1, IV [4]). 2. $Na_2SO_4-K_2SO_4$ — a continuous series of solid solutions with minimum at 25% K_2SO_4, and 832°;, the solid solutions decomposed at 476° to form a compound 1 : 1 [3] (Fig. 1,I).

3. $Na_2Cl_2-Na_2SO_4$ – eutectic at 35% Na_2Cl_2 and 628° [5] (Fig. 1, III). 4. $K_2Cl_2-K_2SO_4$ – a eutectic at 690° and 42% K_2SO_4 [1,6] (Fig. 1, II).
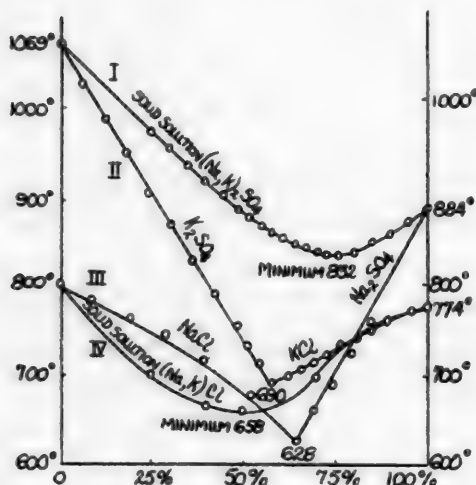
Fig. 1. Lateral binary systems.
I - $K_2SO_4-Na_2SO_4$, II - $K_2SO_4-K_2Cl_2$, III - $Na_2Cl_2-Na_2SO_4$,
IV - $Na_2Cl_2-K_2Cl_2$.
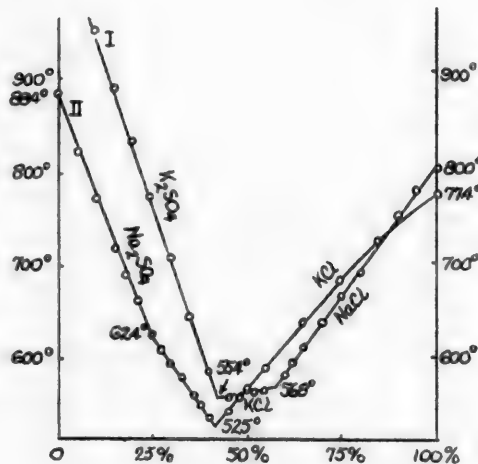
Fig. 2. Diagonal sections of the interrelated system.
I - $Na_2Cl_2-K_2SO_4$, II - $Na_2SO_4-K_2Cl_2$.

Diagonal Cross Sections . $Na_2Cl_2-K_2SO_4$, the unstable corss-section (Fig. 2, I, Table 2), consists of three branches K_2SO_4, KCl and NaCl, which intersect, respectively, at 57% K_2SO_4 and 554°, 41.5% K_2SO_4 and 568°. $K_2Cl_2-Na_2SO_4$ – an unstable section of the melting curve (Fig. 2, II, Table 2); it intersects the internal field phase. It consists of three branches: Na_2SO_4, [X], KCl, which cross at 624° and 24.6% K_2Cl_2 and at 525° and 41.5% K_2Cl_2.

Internal Sections.

16 internal sections (Figs. 3,4 and 5, Tables 3,4,5) were investigated. The characteristics of the sections are given in Table 6.

The internal field for the system, symbolized by "X", was investigated in detail. It is intersected by 10 internal sections, on which curves the crystallization branch is clearly outlined.

Area "X" is also revealed through the five internal interrelated system of lithium, sodium and potassium sulfates and chlorides. In addition, several sections through the prism were investigated, passing through the volume of the crystallization phase "X", for which curves the reality of this phase was confirmed.

The authors assume that the internal field "X" is the independent phase, a combination of sodium and potassium sulfates which are formed during decomposition of the solid solutions of the sulfates.

Formation temperature for the phase "X" lies within the range 514 to 706° (on the basis of the crystallization branches, Fig. 7), and the composition 1 : 1 which is formed during decomposition of the solid solutions in the binary system $Na_2SO_4-K_2SO_4$ at 476° and cannot, therefore, be attributed to it.

The composition of phase "X" was not determined by the authors; however, it is quite possible that it contains more sodium sulfate, to which was given the definitive composition $3Na_2SO_4 \cdot K_2SO_4$ ("antiglazerite"), or $2Na_2SO_4 \cdot K_2SO_4$, which is in accordance with triangulation of the system. There is given in Fig. 6 a full projection of the Na, K‖Cl, SO_4 system in diagram form, and in Fig. 7 a projection of its crystallization branches on the side toward the $Na_2SO_4-K_2SO_4$ square.

One triple eutectic and two transitional points can be found on the diagram; therefore, by triangulation, the square for the interrelated system should be divided into three phase triangles. To triangulate the system, it is necessary to know the composition of the internal phase "X", which is found to be a binary compound, for which the compositions 3 : 1, or 2 : 1, are satisfactory. The triangulated sections, therefore, will radiate from the lateral side

of the $Na_2SO_4-K_2SO_4$, of composition $2:1$ ($2Na_2SO_4 \cdot K_2SO_4$); they are directed toward the apices of NaCl and of KCl, and divide the square for the interrelated system into 3 phase triangles.

TABLE 2
Unstable Diagonal

$Na_2Cl_2-K_2SO_4$						$K_2Cl_2-Na_2SO_4$			
Na_2Cl_2 (in %)	temperature	Na_2Cl_2 (in %)	temperature	Na_2SO_4 (in %)	temperature	K_2Cl_2 (in %)	temperature	K_2Cl_2 (in %)	temperature
0	1069°	45	556°	70	638°	0	884°	33	578°
10	950	48	558	75	665	5	824	36	560
15	890	50	562	80	694	10	772	38	548
20	832	52	563	85	722	15	718	40	532
25	773	55	565	90	750	18	690	45	540
30	708	60	582	95	776	21	662	50	564
35	645	62	594	100	800	25	624	55	588
40	586	65	610			27	608	65	635
						30	594	70	682
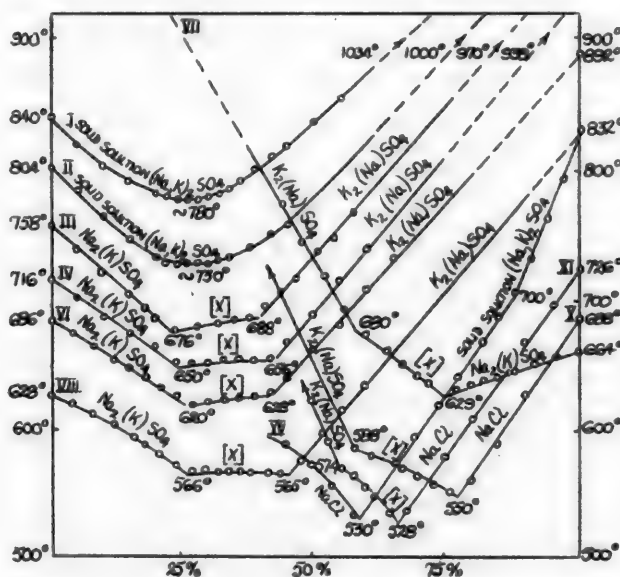
Fig. 3. Internal cross sections through the system.
Roman numerals = cross section numbers,
X = crystallization branch of the internal phase.
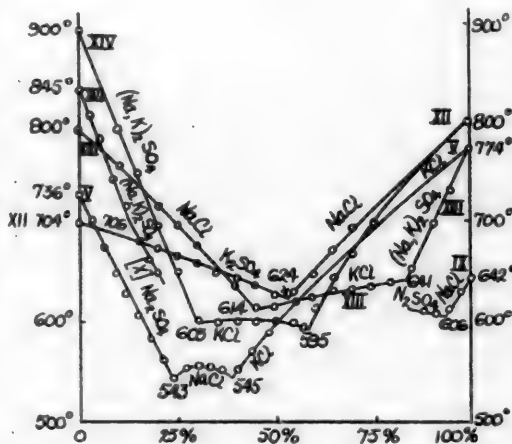
Fig. 4. Internal cross sections through the system.
[X] = crystallization branch of internal phase.

I. $Na_2Cl_2-Na_2SO_4-2Na_2SO_4 \cdot K_2SO_4$ with a transition point at 534° and 13.5% Na_2Cl_2, 25.5% K_2Cl_2, 61% Na_2SO_4.

II. $Na_2Cl_2 + 2Na_2SO_4 \cdot K_2SO_4-K_2Cl_2$ with eutectic point at 514° and 2.5% Na_2Cl_2, 39% K_2Cl_2, 58.5% Na_2SO_4.

III. $K_2Cl_2-2Na_2SO_4 \cdot K_2SO_4-K_2SO_4$ with transition point at 538° and 41.5% K_2Cl_2, 53% Na_2SO_4, 5.5% K_2SO_4.

The diagonal sections do not participate in the triangulation; they are found to be unstable, which is also indicated by the transitional thermal effect for the given system; the latter, therefore, according to the classification[7], is found to be a reversibly adiagonal interrelated system. The diagram consists of three main areas of crystallization, among them two areas of solid solutions (Na, K)Cl and (Na, K)$_2$SO$_4$, of which the first decomposes within the system into the components, and the second with formation of an inner phase "X". The largest areas are occupied by solid solutions of chloride and their decomposition products.

Decomposition of solid solutions occurs on the basis of crystallization branches for the chlorides at 622° and for the sulfates at 706°.

TABLE 3

	Cross section								
I		**II**		**III**		**IV**		**V**	
5% K$_2$Cl$_2$ + 95% K$_2$SO$_4$ (in %)	temp.	10% K$_2$Cl$_2$ + 90% K$_2$SO$_4$ (in %)	temp.	15% K$_2$Cl$_2$ + 85% K$_2$SO$_4$ (in %)	temp.	20% K$_2$Cl$_2$ + 80% K$_2$SO$_4$ (in %)	temp.	K$_2$Cl$_2$ (in %)	temp.
0	840°	0	804°	0	758°	0	716°	0	736°
5	820	5	784	5	740	5	702	3	705
10	804	10	764	10	724	10	688	6	678
15	794	15	748	15	706	15	674	9	652
20	783	20	733	18	696	20	664	12	630
22	782	22	730	20	687	24	653	15	608
24	780	24	730	24	678	27	650	18	586
26	780	26	730	28	681	30	652	21	564
28	780	28	731	32	684	33	653	24	542
30	781	30	731	35	686	36	654	27	554
32	784	32	732	38	688	39	655	30	558
34	788	34	735	41	696	42	658	33	556
36	794	36	738	44	708	45	668	36	554
39	802	38	742	48	718	50	690	40	556
42	812	42	752	50	732	55	714	44	573
45	820	45	760	54	750	60	740	49	590
50	837			58	570	100	938		
55	856								
100	1034								

TABLE 4

	Cross section										
VI		**VII**		**VIII**		**IX**		**X**		**XVI**	
25% K$_2$Cl$_2$ + 75% K$_2$SO$_4$ (in %)	temp.	K$_2$SO$_4$ (in %)	temp.	35% K$_2$Cl$_2$ + 65% K$_2$SO$_4$ (in %)	temp.	K$_2$SO$_4$ (in %)	temp.	K$_2$SO$_4$ (in %)	temp.	37% Na$_2$Cl$_2$ + 63% K$_2$Cl$_2$ (in %)	temp.
0	686°	0	664°	0	828°	0	642°	0	688°	0	841°
4	674	4	657	8	612	3	628	5	654	3	814
8	664	8	652	16	593	6	610	10	626	6	787
12	654	12	646	18	588	9	608	15	590	9	750
15	646	15	642	21	580	12	610	20	562	12	720
18	640	18	638	24	572			24	552	15	686
21	634	20	635	27	562			27	558	18	666
24	626	23	632	30	566			30	564	20	652
27	620	28	637	32	566			33	568		
30	621	30	643	34	565			36	574		
33	622	33	652	38	565			39	580		
36	624	36	661	41	564			42	584		
39	626	40	674	44	563			45	614		
42	628	44	694	48	580			50	654		
45	641	48	720	52	596			55	700		
50	662	52	748	56	618			60	740		
55	684	56	776	60	638			100	1069		
60	708	100	1069	65	658						
65	730			100	832						
100	892										

TABLE 5

	Cross section								
	XI		XII		XIII		XIV		XV	
K_2SO_4 (in %)	temp.	Na_2Cl_2 (in %)	temp.	Na_2Cl_2 (in %)	temp.	Na_2Cl_2 (in %)	temp.	30% K_2Cl_2 + 70% $NaCl_2$ (in %)	temp.
0	726°	0	704°	0	774°	0	900°	0	832°
5	696	10	692	5	736	5	850	3	794
10	668	15	686	10	696	10	800	6	783
15	640	20	678	15	674	15	754	9	732
20	606	25	670	20	640	20	700	12	706
25	580	30	662	25	636	25	654	15	688
28	560	35	652	30	633	30	603	18	668
32	536	40	644	35	630	35	602	22	644
35	534	45	636	40	626	40	603	26	620
38	550	50	628	45	622	45	602	30	595
40	556	55	630	50	618	50	601	34	572
42	564	60	648	55	614	55	598	38	548
44	570	65	672	60	637	60	614	42	532
47	590	70	694	65	656	65	644	46	556
50	625	100	800	70	680	70	670	50	572
55	676			75	700	75	700	55	588
60	723			80	720				

Fig. 5. Placement scheme for internal sections.
Roman numerals = number of cross section

Fig. 6. Projection of melting point diagram on composition square of the interrelated system.
Crystallization fields: I - (K)Na_2SO_4, II - NaCl, III - KCl, IV - (Na)K_2SO_4.
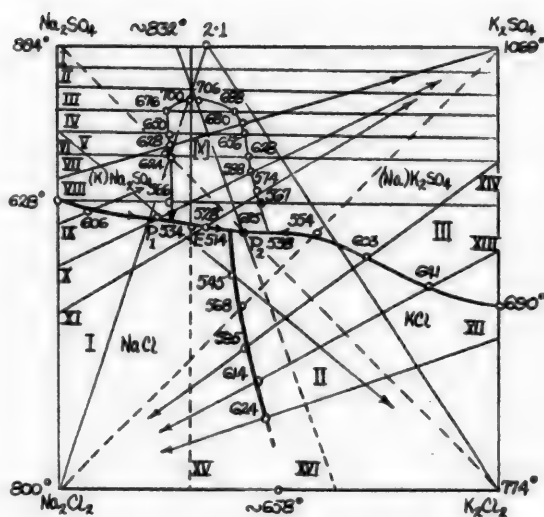
TABLE 6

Cross section number	Initial mixture of components (in %)	Component being added to a mixture of the components (in %)	Branches of the crystallization curves and their intersections						
			I Intersection	%*	Temperature	II Intersection	%	Temperature	III
I	$5Na_2Cl_2 + 95Na_2SO_4$	$5K_2Cl_2 + 95K_2SO_4$	$(Na,K)_2SO_4$ minimum	27	780°				
II	$10Na_2Cl_2 + 90Na_2SO_4$	$10K_2Cl_2 + 90K_2SO_4$	$(Na,K)_2SO_4$ minimum	28	730				
III	$15Na_2Cl_2 + 85Na_2SO_4$	$15KCl + 85K_2SO_4$	$Na_2(K)SO_4$	24	676	[X]	40	688°	$K_2(Na)SO_4$
IV	$20Na_2Cl_2 + 80Na_2SO_4$	$20K_2Cl_2 + 80K_2SO_4$	$Na_2(K)SO_4$	25	650	[X]	42	656	$K_2(Na)SO_4$
V	$20Na_2Cl_2 + 80Na_2SO_4$	KCl	$Na_2(K)SO_4$	24	543	NaCl	38.5	545	KCl
VI	$25Na_2Cl_2 + 75Na_2SO_4$	$25K_2Cl_2 + 75K_2SO_4$	$Na_2(K)SO_4$	26.5	620	[X]	43	628	KCl
VII	$30Na_2Cl_2 + 70Na_2SO_4$	K_2SO_4	$Na_2(K)SO_4$	25	629	[X]	42	680	KCl
VIII	$35Na_2Cl_2 + 65Na_2SO_4$	$35KCl + 65K_2SO_4$	$Na_2(K)SO_4$	26	566	[X]	45.5	565	KCl
IX	$40Na_2Cl_2 + 60Na_2SO_4$	K_2SO_4	K_2SO_4	6.5	606	$Na_2(K)SO_4$	42.5	588	$K_2(Na)SO_4$
X	$50Na_2Cl_2 + 50Na_2SO_4$	NaCl	NaCl	22.5	550	[X]	40.3	574	$K_2(Na)SO_4$
XI	$60Na_2Cl_2 + 40Na_2SO_4$	NaCl	NaCl	33.5	528	[X]			$K_2(Na)SO_4$
XII	$65K_2Cl_2 + 35K_2SO_4$	NaCl	KCl	53	624	NaCl	55	614	NaCl
XIII	$45K_2Cl_2 + 55K_2SO_4$	NaCl	$K_2(Na)SO_4$	16.5	641	KCl	58	595	NaCl
XIV	$25K_2Cl_2 + 75K_2SO_4$	NaCl	$K_2(Na)SO_4$	30	603	KCl	36	530	NaCl
XV	$70Na_2SO_4 + 30K_2SO_4$	$30K_2Cl_2 + 70Na_2Cl_2$	$(Na,K)_2SO_4$	12.5	700	[X]			NaCl
XVI	$28Na_2SO_4 + 72K_2SO_4$	$37K_2Cl_2 + 63Na_2Cl_2$	$(Na,K)_2SO_4$	12.5	706	[X]			NaCl

• Percentage of component or of mixture added.

Fig. 7. Projection of crystallization branches of the interrelated system toward the square of compositions $Na_2SO_4-K_2SO_4$.

a = the solid solutions $(Na, K)_2SO_4$, b = KCl, c = NaCl, d = Na_2SO_4, "X" = internal phase of the system, E = eutectic, P_1 and P_2 = transition points

SUMMARY

1. The Na, K‖Cl, SO_4 system, with a conditional thermal effect of 0.38 kcal per gram equiv. for the exchange reaction, toward $Na_2Cl_2 + K_2SO_4$, is found to be a reversible adiagonal interrelated system upon triangulation, starting from the pole of composition of the $2Na_2SO_4 \cdot K_2SO_4$ or the $3Na_2SO_4 \cdot K_2SO_4$ compound.

2. There has been found within the system a crystallization area of independent phase, found to be a binary compound of sodium and potassium sulfates, formed by decomposition of solid solutions of $Na_2SO_4-K_2SO_4$ binary system sulfates.

3. There are found in the system: one ternary eutectic point at $514°$ and 2.5% Na_2Cl_2, 39% K_2Cl_2, 58.5% Na_2SO_4 and two triple transitional points. By triangulation, the square for the interrelated system is divided into 3 phase triangles.

4. A diagram of the system consists of three major crystallization fields, amidst two continuous solid solutions, $(Na, K)Cl$ and $(Na, K)_2SO_4$, which decompose within the system: chlorides at $622°$ form the components, and sulfates at $706°$ form the compounds, of hypothetical compositions 3 : 1 and 2 : 1.

5. A diagram for the system Na, K‖Cl, SO_4, investigated by the authors, differs completely from the diagram given by Jänecke.

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PHYSICO-CHEMICAL INVESTIGATION OF THE SYSTEM

KBr - AlBr₃ - NITROBENZENE

(SPECIFIC GRAVITY, VISCOSITY AND CRYOSCOPY)

T. E. Koval

Ternary systems consisting of aluminum halides, alkali metal halides and an organic solvent, and in particular, the KBr· AlBr₃ – nitrobenzene system, have, many times, been the objects of physico-chemical investigation of such anhydrous solutions.

Plotnikov and his school obtained voluminous material on the electroconductivity, electrolysis, decomposition potentials and molecular state [1-13] while studying the above-indicated system, wherein they gave data indicating formation of complex compounds from components of the system, while other authors gave the compositions of the complexes and schemes for their electrolytic dissociation. It should be mentioned, however, that deductions about the compositions of complex compounds, particularly about their electrolytic dissociations, are in many cases only hypothetical, because they are based upon a limited amount of data on physico-chemical properties.

In connection with the above-indicated facts, the authors have attempted to clarify compositions of the complex compounds and of ion formation in the KBr· AlBr₃ –Nitrobenzene system, on the basis of specific gravity, viscosity and cryoscopic study, including data on electroconductivity, transference numbers and electrolysis data which are to be found in the literature [1,5].

EXPERIMENTAL

<u>Initial Compounds and Methods of Measurement.</u>   Aluminum bromide was prepared according to the Gustavson method [14], from aluminum shavings and bromine, and was then distilled repeatedly and stored in sealed flasks. Potassium bromide was crystallized from aqueous solution, and then dried and stored in a dessicator. Nitrobenzene was prepared according to the Gatterman method [15] from benzene which was thoroughly purified beforehand, and the former purified by repeated washing with water, followed by soda solution, and then with water, dried over calcium chloride, distilled, and stored in sealed flasks.

All solutions were prepared in such manner that for all cases the ratio of aluminum bromide to nitrobenzene remained constant, with variation in amount of potassium bromide in the solution.

Since aluminum bromide hydrolysis can affect drastically the results of measurements, the authors directed their attention to the problem of protecting the solution from moisture during preparation and work with same, all measurements being carried out in containers and apparatus with hermetic seals.

Specific gravity was determined in standard manner by pycnometer in a thermostat at 20°. Viscosity measurements on the solution at 20° were carried out in an Ostwald viscometer of modified construction for the use of anhydrous solutions, permitting a satisfactory insulation of solution from air moisture during measurements. Cryoscopic measurements were carried out in standard form, using a Beckman apparatus with electro-magnetic stirrer. The solution under investigation was insulated in the Beckman apparatus from external air by means of a well-ground stopper and a ground connection through which the thermometer was introduced into the container.

Measurement Results and Their Evaluation

The insolubility of KBr in nitrobenzene, and its solubility, with heat evolution, in nitrobenzene solutions of AlBr₃, the increased electroconductivity of nitrobenzene solutions of AlBr₃ upon adding KBr [1-6], undoubtedly indicate complex formation in the system KBr· AlBr₃ –Nitrobenzene.

Sheka and Pechenaya [5], upon studying the transference numbers of ions in the system indicated, came to the conclusion that AlBr₄⁻ is the anion in this system, and that K⁺ and Al⁺⁺⁺ · nC₆H₅NO₂ are the cations. Moreover, this makes possible the existence of complex cations in the solution which contain more than one potassium atom per ion.

On the basis of their results, however, an equally plausible conclusion can be reached concerning formation of a complex compound of the composition KAl_2Br_7, and its dissociation into the cations K^+ and $Al^{+++} \cdot nC_6H_5NO_2$, and the anion Al_2Br_7.

Specific Gravity and Viscosity of The KBr $\cdot$ AlBr$_3$—Nitrobenzene System.

Change in specific gravity and viscosity of the system in relation to the molar ratio $\dfrac{KBr}{AlBr_3}$ in the solution were studied by the authors within the molar ratio range of 0.134 to 1.13. Results of the specific gravity and viscosity measurements for the KBr $\cdot$ AlBr$_3$—nitrobenzene system are given in Table 1, and presented graphically in the form of curves $d = f_1\left(\dfrac{KBr}{AlBr_3}\right)$ and $\eta = f_2\left(\dfrac{KBr}{AlBr_3}\right)$ (Figs. 1 and 2).

As the data of Table 1 indicate, the specific gravity and the viscosity of the system increase gradually with increase in the molar ratio of KBr/ AlBr$_3$ in the solution, ranging from 0.134 to 0.509; they decrease in the range 0.509 to 0.712, and from 0.712 to 0.967 they again increase, reaching a maximum value, and then remaining constant with further increase in molar ratio of $\dfrac{KBr}{AlBr_2}$ in the solution.

TABLE 1

Specific gravity and viscosity for the system KBr $\cdot$ AlBr$_3$—Nitrobenzene
$C_6H_5NO_2$—14.400 g, AlBr$_3$—0.5000 g

Experiment number	KBr (in g)	$\dfrac{KBr}{AlBr_3}$ (in moles)	d	η (in centipoises)
1	-	-	1.2232	2.1173
2	0.0299	0.134	1.2242	2.1141
3	0.0553	0.247	1.2244	2.1268
4	0.0986	0.443	1.2270	2.1314
5	0.1132	0.509	1.2296	2.2546
6	0.1201	0.540	1.2288	2.2059
7	0.1420	0.638	1.2285	2.1345
8	0.1585	0.712	1.2276	2.0297
9	0.1753	0.788	1.2289	2.0464
10	0.1852	0.832	1.2311	2.0937
11	0.2007	0.902	1.2328	2.0965
12	0.2153	0.967	1.2345	2.4791
13	0.2505	1.126	1.2343•	2.4787•
14	0.2517	1.130	1.2345•	2.4791•

It should be mentioned that according to the authors' observation, for molar ratios of $\dfrac{KBr}{AlBr} > 0.967$, potassium bromide is almost insoluble in a nitrobenzene solution of aluminum bromide, i.e., it ceases to interact with aluminum bromide, and the solution becomes saturated with respect to potassium bromide.

It can be seen from Figs. 1 and 2 that two maxima and one minimum, individually, can be found on the $d = f_1\left(\dfrac{KBr}{AlBr_3}\right)$ and $\eta = f_2\left(\dfrac{KBr}{AlBr_3}\right)$ curves.

Appearance of the first maximum of molar ratio $\dfrac{KBr}{AlBr_3} = 0.509$ is apparently connected with formation of a complex compound of the composition KAl_2Br_7 in the solution; the appearance of a second maximum of molar ratio $\dfrac{KBr}{AlBr_3} = 0.967$ corresponds to formation of a complex compound of the composition $KAlBr_4$ in the solution, which can be presented schematically by means of equations:

• The solution was saturated with respect to KBr.

$$KBr + (AlBr_3)_2 \rightleftharpoons KAl_2Br_7, \bullet \qquad (1)$$

$$KAl_2Br_7 + KBr \rightleftharpoons 2KAlBr_4. \qquad (2)$$
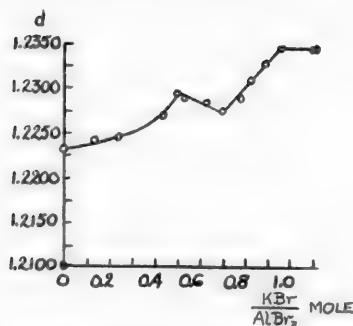
Fig. 1. Specific gravity of the KBr · AlBr₃—Nitrobenzene System.
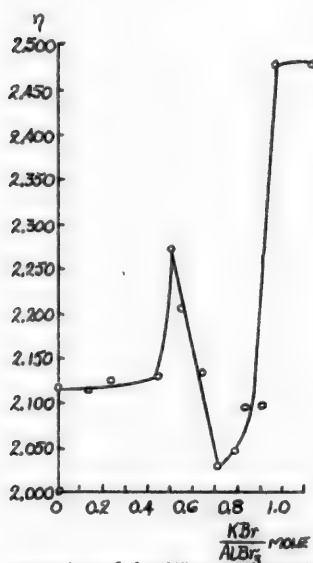
Fig. 2. Viscosity of the KBr· AlBr₃—Nitrobenzene System

The presence of complex compounds of the compositions KAl_2Br_7 and $KAlBr_4$ in solution, for molar ratios $\dfrac{KBr}{AlBr_3}$ equal, respectively, to 0.509 and 0.967, are found to be in full accord with the authors' results from cryoscopic investigation, as well as with the results from electroconductivity measurements [1], and from transference numbers [5].

The appearance of a minimum on the $d = f_1\left(\dfrac{KBr}{AlBr_3}\right)$ and $\eta = f_2\left(\dfrac{KBr}{AlBr_3}\right)$ curves for molar ratio $\dfrac{KBr}{AlBr_3} = 0.712$ is, in the authors' opinion, the result of a reaction occurring in the solution

$$KAl_2Br_7 + KBr \rightleftharpoons 2KAlBr_4,$$

because of which there occurs in solution a substitution of the KAl_2Br_7 molecule for a $KAlBr_4$ molecule.

It can be seen from the reaction equation that, on the one hand, new molecules appear, and on the other hand, upon addition of potassium bromide, two particles of another complex compound of the composition $KAlBr_4$ appear in the solution, instead of one particle of complex compound, having the composition KAl_2Br_7, which leads to a sharp change in concentration of particles in the solution. Two factors, in the main, affect specific gravity and viscosity between the first and second maxima: the 1st factor, which is conditioned by the nature of the newly-formed complex molecules, and the 2nd factor, which is conditioned by the change in concentration of particles in the solution.

The first factor decreases specific gravity and viscosity of the system; the second factor increases these properties. Before the minimum is reached, the first factor evidently dominates over the second; after the minimum is reached, the reverse phenomenon takes place, and minima appear as the result on the $d = f_1\left(\dfrac{KBr}{AlBr_3}\right)$ and $\eta = f_2\left(\dfrac{KBr}{AlBr_3}\right)$ curves. The possibility of solvation of the particles by nitrobenzene during the process is not excluded, which will also be evident in a definitive manner upon changes in viscosity and specific gravity for the system.

Stability in specific gravity and viscosity of the system after the second maximum, for molar ratios of $\dfrac{KBr}{AlBr_3} > 0.967$ is apparently tied up with the fact that KBr no longer enters into reaction with the complex molecules, the solution becoming saturated with respect to it, and hence the concentration of the complex compound in the solution remains constant, which, naturally, will not be evident in change of specific gravity and viscosity of the solution.

In such a situation, the $d = f_1\left(\dfrac{KBr}{AlBr_3}\right)$ and $\eta = f_2\left(\dfrac{KBr}{AlBr_3}\right)$ curves will proceed parallel to the abscissa axis, as was indeed observed by the authors.

_____

• Cryoscopic measurements have indicated that aluminum bromide is found in the form of dimer molecules in nitrobenzene.

Cryoscopy of the KBr·AlBr$_3$—Nitrobenzene System.

For the purpose of a detailed clarification of the problem of complex formation and electrolytic dissociation of complex compounds, for the system KBr· AlBr$_3$ —nitrobenzene, the authors carried out cryoscopic measurements of the solution with molar ratios $\dfrac{KBr}{AlBr_3}$ over the range of 0.166 to 1.130 (Table 2, Figs. 3 and 4).

TABLE 2
Cryoscopy of KBr AlBr$_3$—Nitrobenzene System
C$_6$H$_5$NO$_2$ — 14.400 g

Expt. no.	AlBr$_3$ (in g)	KBr (in g)	Molar ratio $\frac{KBr}{AlBr_3}$	t_0	t_1	t_2	Δt	Δt_1	Δt_2	M_{AlBr_3}	M_{KBr}	$M_{complex}$
1	—	—	—	5.503								
2	0.5000	—	—		4.782		0.721			331.811		
3	0.5000	0.0379	0.166			4.634		0.148	0.869		122.500	251.400
4	0.5000	0.0420	0.187			4.615		0.167	0.888		120.338	221.000
5	0.5000	0.1050	0.471			4.378		0.424	1.125		118.200	246.800
6	0.5000	0.1190	0.535			4.307		0.475	1.196		119.869	218.400
7	0.5000	0.1540	0.690			4.161		0.621	1.342		118.700	214.100
8	0.5000	0.1699	0.765			4.095		0.687	1.408		118.710	213.100
9	0.5000	0.1928	0.866			3.977		0.805	1.526		114.595	209.600
10	0.5000	0.2043	0.912			3.957		0.825	1.546		118.487	213.300
11	0.5000	0.2090	0.941			3.935		0.843	1.568		118.710	213.000
12	0.5000	0.2146	0.960			3.915		0.867	1.588		118.000	212.900
13	0.5000	0.2505	1 126			3.910		0.872	1.593		Molecular weight of KBr and the complex was not determined*	
14	0.5000	0.2517	1.130			3.916		0.866	1.587			

t_0 = freezing temperature of nitrobenzene
t_1 = freezing temperature of nitrobenzene solution of aluminum bromide
t_2 = freezing temperature of nitrobenzene solution of potassium bromide and aluminum bromide.
$t_0 - t_1 = \Delta t$ = lowering of freezing point of nitrobenzene solution of aluminum ·· bromide
$t_1 - t_2 = \Delta t_1$ = lowering of freezing point of potassium· ·bromide solution in nitrobenzene solution of aluminum· bromide
$t_0 - t_2 = \Delta t_2$ = lowering of freezing temperature of potassium bromide nitrobenzene solution and aluminum-bromide nitrobenzene solution
M_{AlBr_3} = molecular weight of the aluminum bromide
M_{KBr} = molecular weight of the potassium bromide
$M_{complex}$ = molecular weight of the complex compound

Molecular weights were calculated according to a standard formula; cryoscopic constant for nitrobenzene was adopted as 6.89.

It can be seen from the data of Table 2 that the experimental M_{AlBr_3} = 331.811, while the theoretical was M_{AlBr_3} = 266.73. Thus, the experimental molecular weight of aluminum bromide was found to be higher than the theoretical weight corresponding to monomeric molecules, and lower than the theoretical corresponding to dimer molecules. Taking into account the relatively good electroconductivity of aluminum bromide nitrobenzene solution, indicative of electrolytic dissociation of aluminum bromide [6, 7], the authors concluded that aluminum bromide in nitrobenzene is in the form of dimer molecules.

It can also be seen from the data of Table 2 that upon increasing the amount of potassium bromide in the solution, the freezing temperature of the aluminum bromide and the potassium bromide in nitrobenzene solution decreases,
* Solution was saturated with respect to KBr and the complex compound.

and the freezing point lowering increases.

The effect of potassium bromide upon freezing point lowering of aluminum bromide nitrobenzene solution is presented graphically in the form of curves $\Delta t_1 = f_3\left(\dfrac{KBr}{AlBr_3}\right)$ and $\Delta t_2 = f\left(\dfrac{KBr}{AlBr_3}\right)$ in Figs. 3 and 4.

The curves indicate that there exists a direct relationship between the freezing point lowering for the solution and the molar ratios of $\dfrac{KBr}{AlBr_3}$, which breaks down with molar ratios of $\dfrac{KBr}{AlBr_3} > 0.967$.

The rectilinear character of curves $\Delta t_1 = f_3\left(\dfrac{KBr}{AlBr_3}\right)$ and $\Delta t_2 = f\left(\dfrac{KBr}{AlBr_3}\right)$ is evidently related to the fact that potassium bromide combines with aluminum bromide in nitrobenzene; because of this fact, therefore, complex compounds are formed with a degree of electrolytic dissociation which is greater than the degree of dissociation of aluminum bromide dimer molecules, i.e., there occurs in the solution a replacement of molecules which are less dissociated by those of more dissociated complex molecules, and hence the concentration of particles in the solution increases, and thus the freezing point lowered as the result.

The above-given hypothesis has been fully confirmed by the author's results according to investigations of specific gravity and electroconductivity of the system, $KBr \cdot AlBr_3$ – nitrobenzene, with respect to a molar ratio of $\dfrac{KBr}{AlBr_3}$ in the solution.

Plotnikov and Gorenbein [1] studied electroconductivity of the $KBr \cdot AlBr_3$ – nitrobenzene system in relation to a molar ratio of $\dfrac{KBr}{AlBr_3}$ within the molar ratio range of 0.103 to 0.861 where for the increased molar ratio of $\dfrac{KBr}{AlBr_3}$ in solution, electroconductivity increases all the time, and the $\kappa = f\left(\dfrac{KBr}{AlBr_3}\right)$ curve has a rectilinear character.

On the basis of cryoscopic measurements, the author has calculated the molecular weight of potassium bromide at various molar ratios of $\dfrac{KBr}{AlBr_3}$ in the solution. It can be seen from the data of Table 2 that the experimental molecular weight of potassium bromide remains almost constant for all of the experimental cases, and almost equal to the theoretical. The theoretical molecular weight of KBr is equal to 119.012, and the experimental value for all investigated cases fluctuated within the range 114.595 to 122.5; the average experimental molecular weight for KBr was equal to 118.81.

Considering that the potassium bromide molecules combine with aluminum bromide molecules, and also the fact that upon electrolysis of the $KBr \cdot AlBr_3$ – nitrobenzene system cations, K^+, are discharged at the cathode, the author believes that the complex compounds formed by potassium and aluminum bromides are dissociated

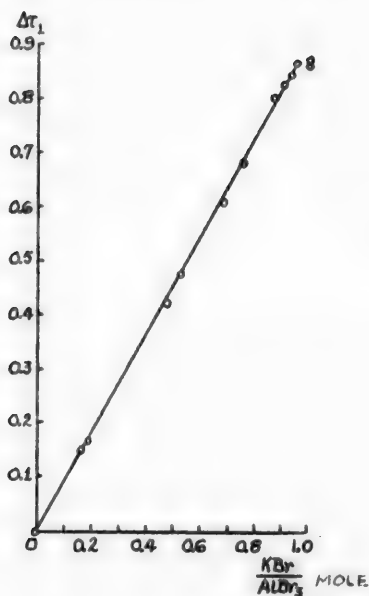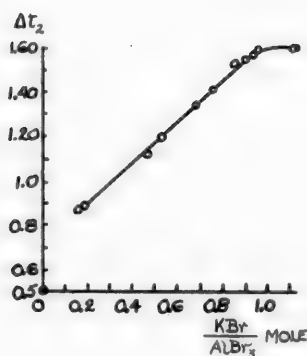Fig. 3. Freezing point lowering of KBr solution in a nitrobenzene solution of $AlBr_3$.

Fig. 4. Freezing point lowering of a nitrobenzene solution of KBr and $AlBr_3$.

in solution, with almost 100% freeing of the K^+ cations. Such a hypothesis completely clarifies the equality between experimental and theoretical molecular weights for potassium bromide in the situation of its combination with aluminum bromide in solution.

Results of the author's measurements of specific gravity and viscosity for the KBr · AlBr$_3$ — nitrobenzene system indicate that for a molar ratio of $\dfrac{KBr}{AlBr_3}$= 0.509 the complex compound KAl$_2$Br$_7$ exists in solution, and with

$\dfrac{KBr}{AlBr_3}$ = 0.967, and higher, KAlBr$_4$.

Cryoscopic measurements indicated that the complex compounds are dissociated into ions in the direction of K$^+$ ion formation, almost 100%.

Proceeding from the above-indicated, the process of complex compound electrolytic dissociation can be presented in the form of the following equations:

$$KAl_2Br_7 \rightleftharpoons K^+ + Al_2Br_7^-,$$

$$KAlBr_4 \rightleftharpoons K^+ + AlBr_4,$$

with the degree of dissociation close to unity.

In order to clarify the problem of the presence of other ions in the solution, the author carried out calculations of molecular weights for complex compounds on the basis of his own cryoscopic data (Table 2).

As can be seen from the data of Table 2, the experimental molecular weight for the complex compound KAl$_2$Br$_7$ fluctuates within the range of 221 - 251.4; the average experimental, however, is equal to 239.73; the complex compound KAlBr$_4$ fluctuates within the range 209.6 - 218.4, the average experimental value being 213.49.

The theoretical molecular weight of KAl$_2$Br$_7$ is equal to 652.448, and of KAlBr$_4$, 385.73.

If a comparison is made of the experimental molecular weights for the complex compounds KAl$_2$Br$_7$ and KAlBr$_4$ with the theoretical, for compound KAl$_2$Br$_7$ the experimental molecular weight is approximately 2.7 fold less than the theoretical, while for the compound KAlBr$_4$ it is approximately 1.85 fold less than the theoretical.

With regards to the above-indicated, the author has come to the conclusion that KAlBr$_4$ is dissociated into two ions, the K$^+$ cation and the AlBr$_4^-$ anion, with the extent of dissociation close to unity.

With respect to the complex compound KAl$_2$Br$_7$, the latter is apparently dissociated on the whole into the cation K$^+$ and the anion Al$_2$Br$_7^-$, but the existence of other ions in the solution must be admitted, since, during dissociation of the two ions, the experimental molecular weight, as compared with the theoretical (even with 100% dissociation) would be 2-dolf less, when according to the author's data, it was found to be 2.7-fold less.

The fact that other ions exist in the solution besides the K$^+$ cation and the Al$_2$Br$_7^-$ anion, is confirmed by results obtained by Sheka and Pechenaya, from a study of the transference numbers for the KBr · AlBr$_3$ — nitrobenzene system. According to their results, the sum of the transference numbers for the cation K$^+$ and the anion AlBr$_4^-$ (or the equivalent Al$_2$Br$_7^-$ anion), is considerably less than unity, which cannot occur during dissociation of a substance into two ions.

Sheka and Pechenaya consider that in solution, apart from the K$^+$ cation and AlBr$_4^-$ anion, there are complex cations present which contain more than one potassium atom per ion.

The author's results, according to cryoscopic investigation of the KBr · AlBr$_3$ — nitrobenzene system, do not confirm the deductions of Sheka and Pechenayay concerning the presence of ions in the solution which contain more than two potassium atoms per ion. If such ions truly did exist in the KBr · AlBr$_3$ — nitrobenzene system, then the molecular weight of potassium bromide could not be equal to the theoretical, as was obtained experimentally by the present author. More probable, in the author's opinion, is the hypothesis that there occurs in solution partial dissociation of the complex Al$_2$Br$_7^-$ anion into more simple ions, according to the equation

$$Al_2Br_7^- \rightleftharpoons Al^{+++} + AlBr_7^{----},$$
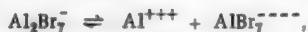
resulting from which is the fact that the sum of the transference numbers, calculated for two ions, is considerably less than unity, and the experimental molecular weight for the compound, KAl$_2$Br$_7$ is 2.7-fold less than the theoretical.

SUMMARY

1. Aluminum bromide in nitrobenzene is found to be in the form of dimeric molecules, (AlBr$_3$)$_2$, partially dissociated into ions.

2. A study of cryoscopy, specific gravity and viscosity indicates the fact that potassium bromide forms two complex compounds with aluminum bromide: with a molar ratio $\dfrac{KBr}{AlBr_3}$ = 0.509, compound of the composition KAl$_2$Br$_7$;

and with a molar ratio $\dfrac{KBr}{AlBr_3} = 0.967$, compound of the composition $KAlBr_4$.

3. Equality of the experimental molecular weight with the theoretical for potassium bromide, and also the fact that during the electrolytic process, potassium cation is discharged on the cathode, indicate almost complete dissociation of the $KAlBr_4$ and KAl_2Br_7 compound into ions in the direction of K^+ cation formation.

4. Results of determination of the molecular weight of complex compounds signify that the compound $KAlBr_4$ in solution is dissociated into the K^+ cation and the $AlBr_4^-$ anion, the compound KAl_2Br_7 being dissociated into the K^+ cation and the $Al_2Br_7^-$ anion.

With respect to the fact that the sum of the transference numbers calculated for two ions is considerably less than the theoretical for the compound KAl_2Br_7, it must be admitted that there is partial dissociation of the $Al_2Br_7^-$ anion into the Al^{+++} cation and the $AlBr_7^{----}$ anion.

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HEAT OF DILUTION OF DIOXAN AND WATER

N. N. Feodosyev, O. A. Osipov and G. K. Morozova

The dioxan – water system has been studied for surface tension, density, vapor pressure, refractive index and freezing point [1]. None of the property-composition diagrams, except that for density, offer information about formation of compounds of the components in this system, However, the density isotherm shows a clearly defined maximum at 32 mole % of dioxan, which may be related to the formation of a hydrate type compound.

Taking the foregoing as a starting point, we undertook to study the heat of dilution of the dioxan – water system.

The heat of dilution was measured in a calorimeter with isothermic shield, as described previously [2].

The components, weighed out in calculated quantities, were placed in two communicating glass vessels in the calorimetric liquid. They were mixed at the appropriate moment, being transferred from vessel to vessel by air pressure. The temperature in the calorimeter was measured to an accuracy of 0.001° by an ordinary metastatic thermometer. Correction for heat exchange was computed by the Regnaud-Pfaundler-Usov equation. The heat value of the calorimeter system was determined after each experiment by dissolving potassium chloride in the calorimeter water.

Purification of the components of the system under study was performed as follows.

After extraction over anhydrous calcium chloride, the dioxan was distilled. The distillate, which condensed in the 99.6-100.5° interval, was glaciated at 4-7°. The crystals were liberated from the liquid phase by means of a Buchner funnel and transferred to a flask with metallic sodium. After three days the dioxan was distilled (in the 100.1-100.8° interval). The pure dioxan froze completely at 12.2°, which is close to the figure given in the literature [1].

The table presents the results of determination of the heat of dilution of the dioxan-water system.• The figure represents a diagram plotted on the numerical data in the table.
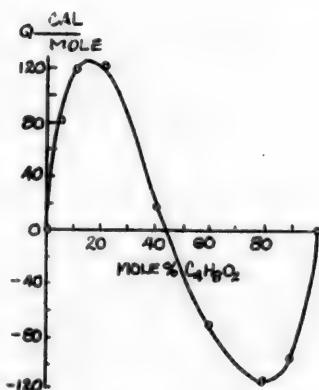
Variation of heat of dilution of dioxan and water with content of dioxan.

Heat of Dilution of Dioxan and Water

Dioxan (mole %)	Heat of dilution, in calories per one mole of mixture
0.0	0.0
5.0	80.6
10.0	118.1
20.0	121.4
40.0	16.5
60.0	−69.6
70.0	−99.6
80.0	−112.0
90.0	−94.8
100.0	0.0

• The heats of dilution of this system were studied at the suggestion of N. A. Trifonov and M. Z. Tsinin.

It is clear from the figure that the curve of heats of dilution for this system is S-shaped, and that the portion of the curve corresponding to high concentrations of dioxan lies below the axis of the mixture.

According to the usual system of classification, this type of curve reflects the occurrence of two simultaneous processes, to wit, the decomposition of associated molecules, accompanied by a negative thermal effect, and the formation of a compound, partially dissociated in the liquid phase, accompanied by a positive effect. Similar isotherms for heat of dilution have been obtained by E. and M. Bose [3], for system consisting of water and ethyl or propyl alcohols.

As the dimolar moment of the dioxan molecule is about 0.4 D, and that of water is 1.84 D, it must be assumed that the negative portion of the curve corresponds to the decomposition of the associated water molecules upon dilution. The positive portion of the curve is related in all probability to the interaction of the components, with the formation of a complex of low thermal stability. This reaction between dioxan and water apparently amounts to the formation of intermolecular hydrogen bonds of the type
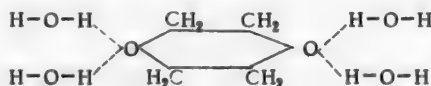
The fact that dioxan readily gives oxonium compounds, and reacts with bromine, iodine and sulfuric acid to form solid crystalline substances is well known. Favorsky describes their structure by means of a formula in which oxygen is tetravalent [4].

SUMMARY

In a dioxan-water system the isotherm of heat of dilution has positive and negative segments, which may be explained by the formation of a molecular compound of water and dioxan of the hydrate type, and the decomposition of an associated component —water.

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EXCHANGE OF BOUND RADICALS BY FREE RADICALS
AND IONS IN SOLUTION

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The behavior of free radicals in solution has been inadequately studied. In particular, very little is known concerning the possibility of their exchange reactions of the type:

$$R_1 \cdot + :X-R \rightarrow R_1-X: + R\cdot. \tag{1}$$

It might be expected that such reactions would not proceed with too great a difficulty since, by analogy with hydrogen isotope exchange, it could be accomplished by the approach of R_1 toward the free electron pair, with simultaneous withdrawal of $R \cdot$, which, apparently, requires only a small activation energy. Exchange reaction for positive ions whose formation as intermediate products is frequently postulated, should, one would think, proceed in analogous fashion, but with greater ease.

Existence of a reaction of the type mentioned was proposed by Kharasch and coworkers [1] for the case of interaction of free methyl with diethyl ether, and by Nesmeyanov and Makarova [2], Kursanov and Setkina [3], for some reactions where positive ions participate.

A study of the exchange reaction of free radicals · of positive organic ions is of great interest for the understanding of chemical process mechanisms. Such data have an added significance, where, for $R_1 = R$ exchange is initiated by chains, which ensures an increase in concentration of radical $R \cdot$, which can play an important role in directing the radical reaction in the required direction.

In the present work the possibility of, and conditions for, an exchange reaction of type (1), for $R_1 = R$, with deuterium labelled free phenyl, ethyl and methyl radicals, and the positive phenyl ion, have been studied. The isotope method not only makes it possible to study exchange between identical radicals, but also the exchange mechanism in the purest form, and makes possible ready separation of the reaction products.

As the source of phenyl radicals, the thermal decomposition reaction of heavy phenyldiazonium chloride [2], or the photodecomposition of heavy iodobenzene, was used. The source of $C_6D_5^+$ was the decomposition reaction of heavy phenyldiazonium borofluoride [2]. The indicated conversions were carried out in light diphenyl ether, phenetole, bromobenzene or iodobenzene, whose molecules, having free electron pairs, can, according to our postulates, undergo the exchange reaction.

Methyl and ethyl radicals were obtained by photochemical decomposition of heavy methyl iodide or heavy ethyl iodide, and in addition, by interaction of phenylmagnesium bromide with heavy methyl iodide, or heavy ethyl bromide, in the presence of cobalt chloride [1]. These transformations were carried out in anisole, phenetole, diethyl or methylbutyl ether medium, molecules of which contain the methyl or ethyl radicals at an oxygen, and can undergo exchange reaction.

Conditions and results of the experiments carried out are given in the Table.

Neither $C_6H_5^+$ ion, nor the $C_6H_5 \cdot$ radical, which form upon thermal decomposition of diazonium salts (Experiments 1-6), nor the $CH_3 \cdot$ and $C_2H_5 \cdot$ radicals, generated by interaction of phenylmagnesium bromide with alkyl halides in the presence of cobalt chloride (Experiments 10 an 11), nor the $C_6H_5 \cdot$ radical formed by photolysis of iodobenzene (Experiment 7), produce any significant exchange with corresponding radicals bound to oxygen, bromine or iodine.

Only in the case of $CH_3 \cdot$ and $C_2H_5 \cdot$ radicals of photochemical origin (Experiments 8 and 9) was the exchange found to exceed experimental error considerably, and determined with certainty.

The fact was that in a number of cases (Experiments 1, 2, 3, 5, 6), and particularly 8 and 9), despite the absence of any significant exchange, part of the deuterium of the initial heavy component was lost; this can be explained (in the case of Experiment 8) by a side reaction of the following type:

$$C_6H_5OCH_3 + I \cdot \rightarrow C_6H_5O \cdot + CH_3I,$$

in which the forming light methyl iodide dilutes the initial heavy material.

TABLE
Conditions and Results of the Exchange Experiments

Experiment No.	Substances exchanged	Experimental condition (temp. or time of illumination)	Excess water density from burning, in γ units				Percent exchange*
			Initial heavy compound	Calculated for radicals being exchanged, both compounds in equilibrium	Found in the heavy component	Found in the exchanging radical of the light component	
1	$C_6D_5^+$ from 6 g $C_6D_5N_2BF_4$ and 18.3 g C_6H_5Br	about 85°; sec.	1596	339	1412	−2	—
2	$C_6D_5^+$ from 6 g $C_6D_5N_2BF_4$ and 21.4 g C_6H_5I	"	1596	331	1388	10	—
3	$C_6D_5^+$ from 5,6 g $C_6D_5N_2BF_4$ and 12.5 g $(C_6H_5)_2O$	"	1596	263	1488	14	—
4	$C_6D_5\cdot$ from 8,5 g $C_6D_5N_2Cl$ and 22.7 g C_6H_5Br	about 100°; sec	1596	471	1575	40	—
5	$C_6D_5\cdot$ from 4.5 g $C_6D_5N_2Cl$ and 17.6 g C_6H_5I	"	1596	478	1482	35	—
6	$C_6D_5\cdot$ from 4,6 g $C_6D_5N_2Cl$ and 12.7 g $(C_6H_4)_2O$	"	1596	302	1482	13	—
7	7,8 g C_6D_5I and 3.9 g $C_6H_5OCH_3$	Exposure 100 hours	1480	760	1459	24	—
8	6,2 g C_2D_5I and 4.7 g $C_6H_5OC_2H_5$	Exposure 104 hours	1118	569	771	134	24
9	4,8 g CD_3I and 6,0 g $C_6H_5OCH_3$	Exposure 200 hrs.	1593	600	1206	77	13
10	$CD_3\cdot$ and $C_4H_9OCH_3$	70°; sec.	723	ca 112**	571***	28	—
11	$C_2D_5\cdot$ and $C_2H_5OC_2H_5$	34°; sec.	1817	ca,115**	1735***	3	—

*   Calculated according to the deuterium content of light component in the exchange reaction.

**   Approximate calculation, assuming uniform distribution of deuterium between the exchanging ether radical and methane, or ethane + ethylene.

***   In the resulting gas.

The data quoted indicate that the exchange reaction for the radicals studied proceeds with difficulty, and is observed only in rare instances.

The interesting fact of difference in behavior of the methyl and ethyl radicals of photochemical origin and the same radicals which form upon reaction of alkyl halides on phenylmagnesium bromide (Experiments 8,9 and 10,11) should be mentioned.

In conclusion we shall point to the fact that results from Experiments 10,11 and 5 do not agree with the data of Kharasch [1], who has indicated a change between the $CH_3 \cdot$ radicals and diethyl ether, nor with the data of Shaw [5], who found that iodobenzene reacts with $C_6H_5 \cdot$ radicals, producing the compound $C_6H_5-I-C_6H_5$, which should lead to an exchange. Apparently the conclusions reached by the above-mentioned authors, based upon circumstantial evidence, are erroneous.

EXPERIMENTAL

The synthesis of heavy iodobenzene, ethyl bromide, ethyl iodide and methyl iodide have been described in the preceding work [10.

Heavy diazonium salts were prepared from aniline, deuterium labeled in the m-position [6]. The aniline hydrochloride required for synthesis of anhydrous phenyldiazonium chloride [7] was prepared by drying a mixture of the equivalent amounts of heavy aniline and concentrated hydrochloric acid in a vacuum desiccator over alkali. The diazonium salt was prepared directly before use. Phenyldiazonium borofluoride was prepared according to the method described by Nesmeyanov, Kocheshkov and Nady [8].

Thermal Decomposition of Heavy Diazonium Salts in Bromobenzene, Iodobenzene, or Diphenyl Ether Medium

Phenyldiazonium chloride or borofluoride was placed in a three-necked flask equipped with stirrer and mercury seal, thermometer extending to the bottom, and a weighed amount of solvent added, and the reaction mixture heated on a water bath with stirring. Decomposition for the phenyldiazonium chloride began at 85-90°, and for phenyldiazonium borofluoride at 70-75°, degradation being carried out, respectively, at 95-100 and 80-90°, and terminated after 5-30 minutes. Reaction mass was then washed with potash solution, water, dried with $CaCl_2$, and distilled in vacuo, the fluorobenzene being collected in a trap cooled with liquid air. After several fractionations, pure chlorobenzene, or fluorobenzene, and solvent were obtained in a yield of 40-60%. Purity of the resulting compounds was ascertained by specific gravity determination, which indicated that impurities did not exceed 0.5-2%.

The exchange reaction for $C_6H_5 \cdot$ radicals, or for $C_6H_5^+$ ions, produced by decomposition of the diazonium salts, leads to the conclusion that the atomic chlorine or fluorine ions which are forming simultaneously, do not combine with either the heavy radical or the ion, but rather with the light, displaced, according to reaction type (1), from the solvent. In this case, the deuterium content of chlorobenzene or of fluorobenzene becomes less than in the initial diazonium salts. On the other hand, a corresponding amount of deuterium gets into the solvent. Therefore, to answer the question of presence or absence of exchange, the chlorobenzene, diphenyl ether, bromobenzene, or iodobenzene, isolated from the reaction mixture, was burned and the water analyzed for deuterium content. Burning of fluorobenzene was found to be inconvenient since the hydrogen fluoride formed reacted with glass and quartz. Fluorobenzene, therefore, was converted to diphenyl,•it being possible to analyze for deuterium content in the latter case without any difficulty.

Photochemical Decomposition of Heavy Iodobenzene, Methyl Iodide and Ethyl Iodide in Anisole or Phenotole Medium ••

A mixture of methyl iodide or iodobenzene with anisole, or a mixture of ethyl iodide with phenetole, was placed in a quartz flask and illuminated with a quartz lamp PRK-2, (cooling by running water). After cessation of exposure, the reaction mixture was washed with potash, dried, and the initial iodide and solvent isolated by fractionation in vacuo, adequate purity of which was confirmed by specific gravity determination. In all experiments of this series, there was obtained upon distillation a considerable amount of high-boiling substances, appearing upon conversion of the radicals and atomic iodine.

• To convert fluorobenzene into diphenyl, the fluorobenzene was heated with metallic sodium at 100° for several hours [9]. The reaction product was extracted with ether. The residue, after removal from ether, was recrystallized from alcohol, or was sublimed in vacuo. Yield of biphenyl was small. Its m.p. was 67-70°.

•• M. P Yakovleva participated in these experiments.

Compositions of the reaction products was investigated in greater detail in Experiment 8: before opening the sealed flask, its contents were cooled with liquid air, and the mixture of gases evolved upon reheating was collected in a gasometer, in the amount of 265 ml. Gases from the gasometer were passed through a bromine trap, and a substance with b.p. about 131° and d_4^{20} 1.5374 was formed, corresponding to the constants for ethylene bromide, and proving the presence of ethylene in the mixture investigated. The second component (whose volume was found to be about 135 ml.) was apparently ethane. Ethyl iodide was distilled out from the liquid in the flask (in vacuo), and the residue was cooled to −30°. A substance precipitated out, which, after recrystallization from heptane, had a m.p. of 81.3-81.7°, corresponding to the literature data for symmetrical diiodoethane. Analysis of the iodine content confirmed the formation of diiodoethane:

Found % : I 90.18, 90.70. $C_2H_4I_2$. Calculated % : I 90.05.

In this experiment diiodoethane interferes with the isolation of pure phenetole. For decomposition of the diiodoethane, the phenetole fraction was heated with zinc dust before final purification.

We analyzed for deuterium content the water from combustion of iodobenzene and methyl and ethyl iodides, which if reaction (1) proceeds, should contain less deuterium than the initial iodide, and the water from combustion of anisole and phenetole, which, according to reaction (1) should have higher deuterium content.

Possibility of Ethyl and Methyl Radical Exchange with Diethyl and Methylbutyl Ethers

Free radicals in these experiments were generated according to the reaction

$$2C_6H_5MgBr + 2C_2D_5Br(\text{or } 2CD_3I) \rightarrow C_6H_5-C_6H_5 + 2MgBr_2(\text{or } 2MgBrI) + 2C_2D_5 \cdot (\text{or } 2CD_3 \cdot).$$

1.27 g of anhydrous cobalt chloride, 10.9 g of heavy ethyl bromide and 7.5 g of anhydrous diethyl ether (or 0.44 g $CoCl_2$, 5 g of CD_3I and 4.4 g of $C_4H_9OCH_3$) were placed in a three-necked flask. To this mixture was added, dropwise, with stirring, 22.8 g of phenylmagnesium bromide solution in 32.5 g of anhydrous ether (or a solution of 8.5 g of C_6H_5MgBr in 12.5 g of $C_4H_9OCH_3$). Upon pouring the mixture boiled. The evolving gases were passed through a trap cooled to −80°, and were collected in a gasometer. Their volume amounted to 1.85 half-ounces (or 0.55 liters), which corresponded to about 70% yield of theoretical.

The reaction mixture was treated with water, and then all of the liquid from the flask distilled in vacuo by heating on a water bath. The ether layer was separated and was boiled for many hours over metallic sodium and distilled to remove alkyl halide. Test for adequate purity was made by determination of specific gravity.

Ether and the gas mixture were burned and the resulting water analyzed for deuterium content.

In the case of exchange reaction by course (1), water of combustion of the ethers should have increased density. The gaseous products from the experiment with ethyl bromide (Experiment 11) consisted of ethane and ethylene, the amount of deuterium in which, for reaction course (1), should be lower than for initial ethyl bromide. In the experiment with methyl iodide (Experiment 10), the gas consisted principally of methane, formed by rupture of hydrogen from the methyl radicals of the reaction mixture. In a majority of cases the molecule which did not have deuterium gave up hydrogen. Therefore, in the absence of reaction course (1), methane combustion should produce water with a deuterium content approximately 25% lower than for the initial methyl iodide, i.e., water with an excess density of about 543 γ. In the case of exchange reaction (1), the density of water should be lower.

Water resulting from combustion of the compounds isolated from the experiments after addition of a small amount of alkali, was analyzed for deuterium content by the microflotation method, with an accuracy of ± 3%.

SUMMARY

1. Exchange between free phenyl, methyl and ethyl radicals labeled with deuterium and positive phenyl ions, obtained by various means, has been studied, as well as the same radicals which compose the compounds.

2. It has been established that exchange reactions are observed only for free methyl and ethyl of photochemical origin, and do not proceed with the same radicals obtained by other means.

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INTERACTION OF 8-HYDROXYQUINOLINE WITH ORGANIC ACID ANHY-
DRIDES, STUDIED BY THE METHOD OF PHYSICO—CHEMICAL ANALYSIS

D. E. Dionisyev and Z. K. Dzhelomanova

8-Oxyquinoline, as an amphoteric compound, behaves as a base in its reactions with mineral acids and forms addition compounds with them, in which one equivalent of acid combines with one molecule of 8-oxyquinoline [1]. We have shown previously [2] that 8-oxyquinoline reacts with acetic and salicylic acids to form compounds with a component ratio of 1 : 2 (2 molecules of acid), while with monochloracetic and benzoic acids it produces compounds of equimolecular composition, with p-nitrobenzoic acid it produces compounds that melt and dissociate, and with p-oxybenzoic, cinnamic and hydrocinnamic acids it does not form molecular compounds.

It is of interest to clarify how 8-oxyquinoline reacts with anhydrides of organic acids. That was our purpose in studying systems of 8-oxyquinoline and acetic, benzoic and phthalyl anhydrides in terms of fusibility, viscosity and electrical conductivity. We were the first to investigate the given systems. The methodology was the same as that we employed in our earlier studies [3]. Viscosity was expressed in centipoises and concentrations in molecular percentages.

The "pure" grade 8-oxyquinoline employed in this work was several times recrystallized from ethyl alcohol, and had a melting point of 75°, d_4^{80} 1.1594. The acetic anhydride was twice distilled with a fractionating column, and the fraction produced had a boiling point of 138-139°, d_4^{20} 1.082, and a melting point of $^-$72°.

The benzoic anhydride was synthesized from benzoic acid by the action of acetic anhydride in the presence of phosphoric acid as a catalyst. It was purified by solution in benzene and recrystallized in petroleum ether. The melting point of the purified product was 42°, the boiling point 360°, and d_4^{95} 1.139.

The phthalyl anhydride was purified by sublimation and had a melting point of 128° and a boiling point of 284.5°.

8-Oxyquinoline — acetic anhydride system. Results of fusibility studies of this system are shown in Fig. 1 (curve a), of viscosity studies in Fig. 2, and of electrical conductivity studies — in Fig. 3. The fusibility curve has one eutectic point and one maximum. The eutectic point, at a melting point of 41.5° corresponds to 65 mole % of 8-oxyquinoline. The maximum, at a melting point of 55.7°, is reached at 50 mole % of 8-oxyquinoline. It indicates the formation, in the solid phase, of a compound having the following composition $C_9H_7NO \cdot (CH_3CO)_2O$.

Viscosity, η, and electrical conductivity, κ, were measured at 75 and 85°.

Fig. 2. shows the viscosity isotherms to have a convex maximum, corresponding to 55 mole % of 8-oxyquinoline, shifted somewhat to the side of the more viscous component.

The electrical conductivity isotherms show a minimum, corresponding to 50 mole % of 8-oxyquinoline, and two maxima. When electrical conductivity is corrected for viscosity the $\kappa\eta$ minimum does not disappear. The viscosity and electrical conductivity data point to the formation of a compound of 1 : 1 ratio in the liquid phase.

8-Oxyquinoline — benzoic anhydride system. Findings are represented as follows: fusibility in Fig. 1, curve b; viscosity in Fig. 2, and electrical conductivity in Fig. 4.

The results shown in Fig. 1 make it clear that 8-oxyquinoline and benzoic anhydride combine into a compound with a melting point of 103° and a composition of 50 mole % 8-oxyquinoline and 50 mole % benzoic anhydride, the component ratio being 1 : 1. The first eutectic point, with a melting point of 49.5° corresponds to 75 mole % 8-oxyquinoline and the second, with a melting point of 32°, to 9 mole % of oxyquinoline.

Viscosity and electrical conductivity were measured at temperatures of 95 and 105°. The viscosity curves have a single point of inflexion at 50 mole % of 8-oxyquinoline and 50 mole % of benzoic anhydride. The viscosity of

the benzoic anhydride — the more viscous component, is 2.497 centipoises at 95° and 2.097 centipoises at 105°, while the maximum viscosity of the system at 95° is 13.08 centipoises, and at 105°, 8.51 centipoises.
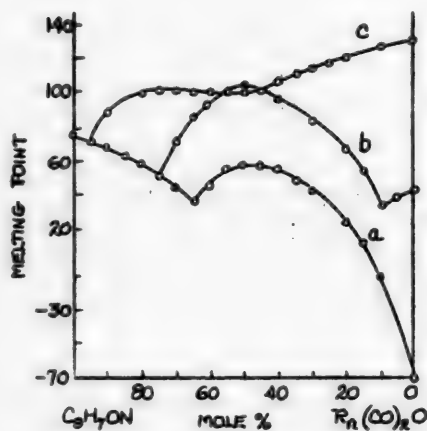
Fig. 1. Explanation in the text.
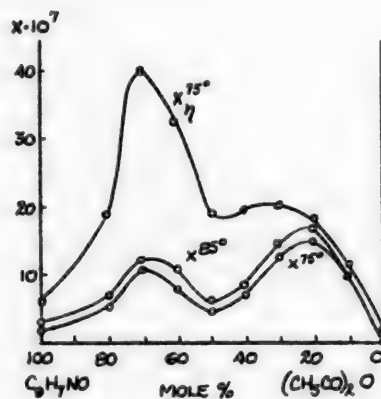
Fig. 3. Explanation in the text.
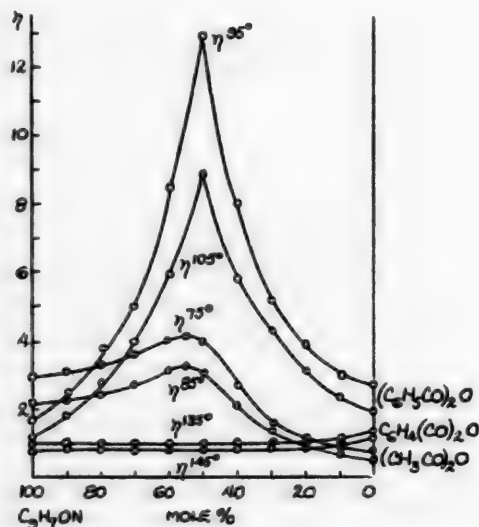
Fig. 2. Explanation in the text
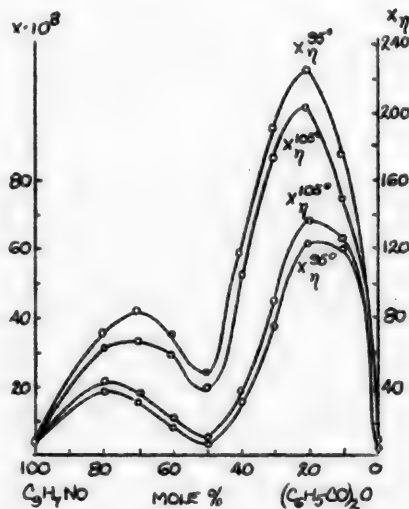
Fig. 4. Explanation in the text.

The electrical conductivity isotherms show a minimum corresponding to 50 mole % of 8-oxyquinoline. When electrical conductivity is corrected for viscosity the minimum neither disappears nor shifts. The liquid phase, too, shows a stable compound of 1 : 1 composition.

8-Oxyquinoline – phthalyl anhydride system. When the fusibility of this system is determined in the usual way, the result is a curve with a eutectic point indicating the absence of a chemical reaction between the components. However, after long heating the fusibility curve (Fig. 1) shows two eutectic points. The first eutectic point, with melting point of 71°, corresponds to 95 mole % of 8-oxyquinoline, and the second, with a melting point of
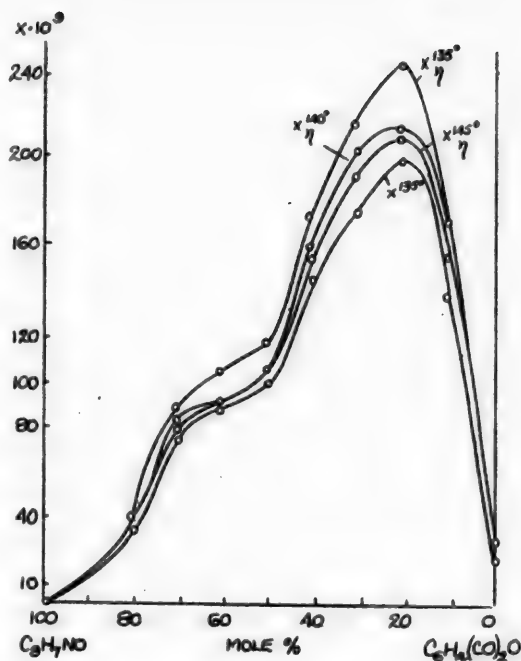
Fig. 5. Explanation in text.
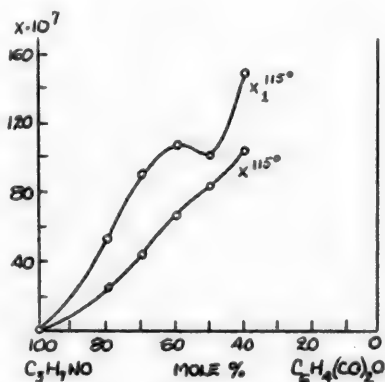
Fig. 6. Explanation in text.

99°, corresponds to 45 mole % of 8-oxyquinoline, indicating the formation of compounds undergoing rapid dissociation.

The viscosity study findings are presented in Fig. 2, and those for electrical conductivity in Figs. 5 and 6. At 135 and 145°, the viscosity curves are somewhat concave in the direction of the composition axis, and give no indication of the occurence of a reaction between the components.

The electrical conductivity curve, κ, determined at 115° (Fig. 6) takes the form of a hyperbola concave toward the composition axis. As temperature rises, the conductivity curves, measured at 135 and 145° (Fig. 5) show points of inflexion corresponding to 50 mole % 8-oxyquinoline. When conductivity is corrected for viscosity the points of inflexion do not disappear.

Conductivity curve κ_1 (Fig. 6) was measured after long-continued heating at 115°. It shows a minimum corresponding to 50 mole % 8-oxyquinoline. Thus, long-continued heating at 115° and heating to 135 and 145° showed reactions between the components in the liquid phase, resulting in a compound of the following formula $C_9H_7NO \cdot C_8H_4O_3$ with a 1 : 1 ratio between its components.

SUMMARY

1. The fusibility, viscosity and electrical conductivity methods were used to study the systems resulting from the reaction of 8-oxyquinoline with acetic, benzoic and phthalyl anhydrides.

2. The curves of viscosity, fusibility and electrical conductivity point to the formation of compounds of the following composition in the solid and liquid phases:

$C_9H_7NO \cdot (CH_3CO)_2O$, $C_9H_7NO \cdot (C_6H_5CO)_2O$ and $C_9H_7NO \cdot C_6H_4(CO)_2O$.
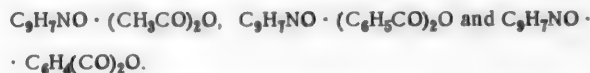
The presence of two phenyl radicals in the anhydride formula facilitates reaction with 8-oxyquinoline, and the viscosity curve of the 8-oxyquinoline —benzoic anhydride system shows a single maximum.

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• T.p. = C.B. Translation pagination.

SYNTHESIS OF HYDROCARBONS

XLV. SYNTHESIS OF CYCLOHEXENE AND CYCLOHEXAND HYDROCARBONS WITH A QUATER-NARY CARBON ATOM, BASED UPON 1,3-DIMETHYL CYCLOHEXADIENE-1,3

R. Ya. Levina, N. P. Shusherina, Kim Dyai Gir and E. G. Treshchova

Our previous communications [1,2] described the reaction we developed as a method of synthesizing ethylene and paraffin hydrocarbons with a quaternary carbon atom. The method embraces two stages: the conversion of a diene hydrocarbon with a conjugate double bond to a tertiary hydrobromide of allyl type with a structure rendering an allyl rearrangement impossible, and the substitution of an organomagnesium compound radical for a free bromine atom in the hydrobromide.

The use in this reaction of 2,4-dimethylpentadiene hydrobromide, a tertiary allyl bromide, resulted in the production of 2,4,4-trimethylalkenes, while hydrogenation of the latter gave 2,4,4-trimethylalkanes [1].

$$CH_3C=CH-C=CH_2 \xrightarrow{+ HBr} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH=C-CH_3 \xrightarrow{+ RMgX} RC-CH=C-CH_3.$$
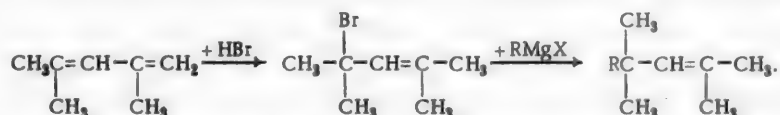
The reaction of another tertiary allyl bromide— 3,5-dimethylheptadiene-2,4 hydrobromide — with organomagnesium compounds was revealed to be a method of synthesizing a second group of hydrocarbons with a quaternary carbon atom —the 3,5-dimethyl-5-ethylalkenes, while their hydrogenation produced 3,5-dimethyl-5-ethylalkanes [2]

$$C_2H_5C=CH-C=CHCH_3 \xrightarrow{+ HBr} C_2H_5C-CH=C-CH_2CH_3 \xrightarrow{+ RMgX} RC-CH=C-C_2H_5.$$
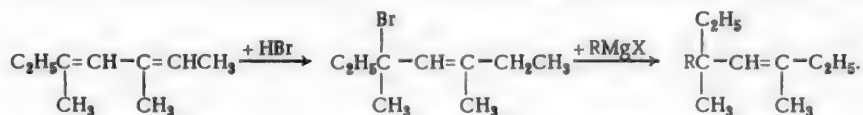
In the present study this method was employed to synthesize cyclohexene and cyclohexane hydrocarbons with a quaternary carbon atom in the ring. The initial diene hydrocarbon was 1,3-dimethylcyclohexadiene-1,3, which was synthesized by reacting methylmagnesium iodide with 1-methyldyclohexen–1-one-3 (ketone cleavage product of methylene-bis-acetoacetic ether) [3]
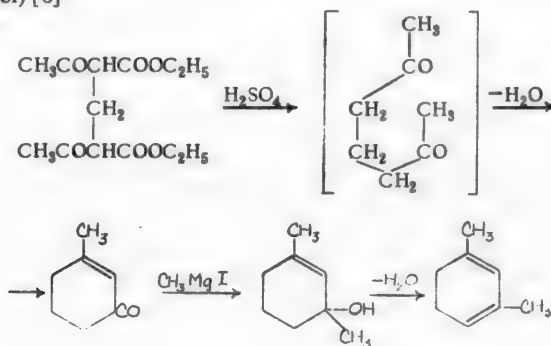
As with the alkadienes we have previously described [1,2], the addition of a single hydrogen bromide molecule to 1,3-dimethylcyclohexadiene follows Markovnikov's law and results in the formation of a tertiary allyl bromide (I), with structure rendering impossible the formation of an isomeric bromide by allyl rearrangement
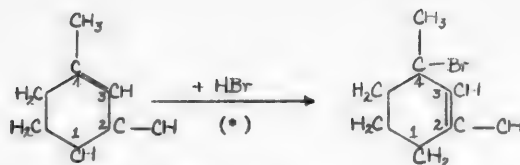
(•) in 1,2 or 1,4 position, according to Markovnikov.

By reacting alkylmagnesium halogenides with that tertiary bromide having a free bromine atom, a number of cyclohexene hydrocarbons with a quaternary atom (Ia) were synthesized: 1,1,3-trimethylcyclohexene-2, 1,3-dimethyl-1-ethylcyclohexene-2 and 1,3-dimethyl-1-propylcyclohexene-2

I   (Ia)   (where R = CH_3, C_2H_5, C_3H_7)
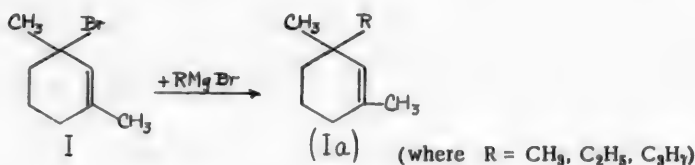
If the addition of hydrogen bromide to dimethylcyclohexadiene also followed the other possible directions (in accordance with and contrary to Markovnikov's law), two more unsaturated allyl bromides (II,III) might be formed in addition to bromide (I).

Bromides (II) and (III), as cyclical analogs of allyl bromide, would react further, at the same time as hydrobromide (I), with the organomagensium compounds, and this might facilitate the formation of the isomeric hydrocarbons (IIa) and (IIIa) as impurities in the main reaction products, the hydrocarbons with a quaternary carbon atom (Ia)

(II)   +RMgX   (IIa)

(III)   (IIIa)
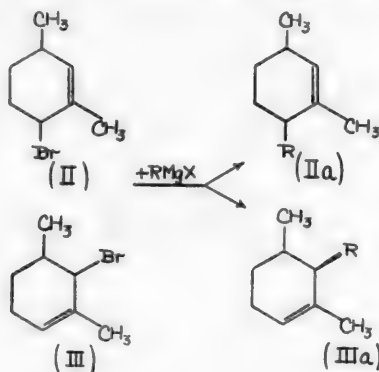
The question as to the purity of the (Ia) sturcture hydrocarbons produced was resolved thus: cyclohexene hydrocarbons with a quaternary carbon atom undergo no change under conditions of irreversible catalysis (Zelinsky's reaction [4]), as one of us had previously shown [5]; however, hydrocarbons (IIa) and (IIIa) should weakly resist this reaction, characteristic of cyclohexene hydrocarbons, and undergo transformation into a mixture of the corresponding cyclohexane and aromatic hydrocarbons
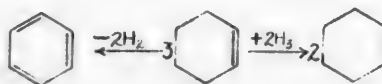
The presence of an aromatic hydrocarbon in the product of catalysis may readily be determined by the Raman spectra.

One of the hydrocarbons we synthesized − 1,3-dimethyl-1-ethylcyclohexene-2 (R=C_2H_5) was passed over platinized charcoal, at 200°, in a weak nitrogen current; the hydrocarbon was recovered unchanged, with the same con-

stants as before catalysis, and readily discolored bromine water; study of the Raman spectra showed complete absence of any admixture of aromatic hydrocarbons.

It was thus established that the cyclohexene hydrocarbons we had produced possessed a quaternary carbon atom in the ring, that this was the reason for their passivity in the given catalytic reaction, and that they contained no admixture of their isomeric hydrocarbons.

Catalytic hydrogenation of the synthesized cyclohexenes resulted in the production of the corresponding cyclohexanes —1,1,3-trimethyl-1,3-dimethyl-1-ethyl- and 1,3-dimethyl-1-propylcyclohexanes. All the lines of maximum and medium intensity in the Raman spectrum of the first of these — 1,1,3-trimethylcyclohexane —corresponded to the lines described in the literature on that hydrocarbon [6,7].

EXPERIMENTAL

1-Methylcyclohexen —1-one-3 (b.p. 198-200° at 750 mm) was prepared with a 60% yield by Knoevenagel's method [3] — reacting dilute sulfuric acid with methylene-bis-acetoacetic ether.

1,3-Dimethylcyclohexadiene-1,3 was synthesized by reacting 1-methyl-cyclohexen —1-one-3 with methylmagnesium iodide as described by us previously to produce 2,4-dimethylpentadiene-1,5 [1]; after distillation in a nitrogen current over sodium, the hydrocarbon (yield 66% of the theoretical) showed the following constants:

B.p. 135-136° at 755 mm, n_D^{20} 1.4872, d_4^{20} 0.8308, MR_D 35.83. C_8H_{14}. Calculated 36.01.

Literature data [8]: b.p. 135-136°, n_D^{20} 1.4856, d_4^{20} 0.8373.

Addition of hydrogen bromide to 1,3-dimethylcyclohexadiene was conducted under chilling by snow and salt; a current of dry hydrogen bromide was passed through the hydrocarbon until the weight gained corresponded to the addition of one molecule of hydrogen bromide (12-12.5 g). Immediately after the hydrobromide was obtained, it was dissolved in an equal volume of ether and reacted with organomagnesium compounds

Reaction of 1,3-dimethylcyclohexadiene-1,3 hydrobromide with alkylmagnesium halogenides (RMgX, where R=CH₃, C₂H₅, C₃H₇) was effected under the conditions previously described by us for other tertiary allyl bromides [1,2], i.e., under a 1 : 1.5 : 1.5 ratio of hydrobromide, alkyl haloid and magnesium with constant stirring and chilling of the reaction to —40 or —50°, and subsequent heating and stirring for six hours. The reaction products — cyclohexene hydrocarbons with a quaternary carbon atom — were distilled with sodium into a column with an efficiency of 25 to 30 theoretical plates; the constants of the hydrocarbons produced (not described in the literature*) and their yields are presented in Table 1.

1,3-Dimethyl-1-ethylcyclohexene-2

5.510 mg substance: 17.521 mg CO_2; 6.532 mg H_2O. 2.957 mg substance: 9.412 mg CO_2; 3.460 mg H_2O. Found %: C 86.78, 86.86; H 13.26, 13.09. $C_{10}H_{18}$. Calculated %: C 86.88; H 13.12.

1,3-dimethyl-1-ethylcyclohexene-2 was subjected to Raman spectra study; the basic frequency of the double bond (1677 cm⁻¹) corresponded to the cyclohexene hydrocarbon with double bond to the alkylated carbon atom.

Relation of 1,3-dimethyl-1-ethylcyclohexene-2 to irreversible catalysis. 1,3-dimethyl-1-ethylcyclohexene-2 was passed through platinized charcoal (15% Pt) in a nitrogen current at 200° (conditions of irreversible catalysis [4]). The produced catalysis products discolored bromine water instantaneously and possessed the constants of the initial hydrocarbon. Study of the Raman spectrum of the catalysis products showed a complete absence of the characteristic lines of aromatic hydrocarbons.

Hydrogenation of the synthesized cyclohexene hydrocarbons with aluminum oxide over nickel at 170° resulted in the production of the corresponding cyclohexane hydrocarbons, possessing the constants shown in Table 2.

The data for 1,1,3-trimethylcyclohexane given in the literature are: Knoevenagel [3] b.p. 137-138°(760mm) n 1.4324, d_4^{15} 0.7848; Fenske [7] b.p. 136.63°, n_D^{20} 1.4296

Table 3 compares the Raman spectra for 1,1,3-trimethylcyclohexane found in the present study with those presented in the literature on that hydrocarbon.

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* The activity of the catalyst in irreversible catalysis was verified before and after the 1,3-dimethyl-1-ethylcyclohexene-2 was passed, by passing cyclohexene.

TABLE 1

Hydrocarbons of the general structure
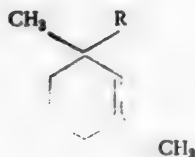
R	Name	Boiling points	n_D^{20}	d_4^{20}	MR$_D$		Yield, % of theoretical
					Found	Calculated	
CH$_3$	1,1,3-Trimethylcyclo-hexene-2	137.5-138.8° (757 mm)	1.4583	0.8123	41.67*	42.19	34
C$_2$H$_5$	1,3-Dimethyl-1-ethyl-cyclohexene-2	164-164.4° (757 mm)	1.4593	0.8278	46.13	45.71	27
C$_3$H$_7$	1,3-Dimethyl-1-propyl-cyclohexene-2	181.5-182.5° (755 mm)	1.4632	0.8260	50.69	50.33	13

TABLE 2

Hydrocarbons of the general structure
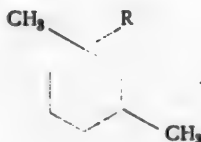
R	Name	Boiling points	n_D^{20}	d_4^{20}	MR$_D$	
					Found	Calculated
CH$_3$	1,1,3-Trimethylcyclo-hexane	135° (758 mm)	1.4318	0.7808	41.83	41.56
C$_2$H$_5$	1,3-Dimethyl-1-ethyl-cyclohexane**	165-165.5° (758 mm)	1.4419	0.8005	46.27	46.18
C$_3$H$_7$	1,3-Dimethyl-1-propyl-cyclohexane	187-188° (751 mm)	1.4467	0.8065	50.99	50.80

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* The 1,1,3-trimethylcyclohexene-2 produced may contain an impurity in the form of the initial dimethylcyclohexadiene, which distills at almost the same temperature (b. p. 135-136°).

** Not described in the literature.

We used a Steinchel spectrograph with the usual 6cm^{-1} slit to obtain the 1,1,3-trimethylcyclohexane spectrum; the line intensity was measured visually, by means of a conventional scale, in which a frequency intensity of 1450 cm^{-1} was taken as 10 units.

TABLE 3

Spectrum of 1,1,3-trimethylcyclohexane

Obtained in present study	Data from the literature	
	[6]	[7]
224 (0.5), 242 (0.3),		
272 (0.5; w), **325 (6)**.	326 (3),	329 (0.062),
355 (0.1), 376 (0.1),	363 (0),	
399 (1.8), 419 (1.8),	401 (1), 419 (0.5),	402 (0.041),
442 (1), **463 (4)**	437 (0.5), 465 (2)	465 (0.062),
499 (0), 537 (0.3),		499 (0.017),
547 (0.1), **556 (12)**,	557 (5),	557 (0.109),
587 (0.1), 621 (0),		
670 (0.5), **726 (20)**,	726 (8),	669 (0.014), 728 (0.163),
769 (0), 797 (2),	797 (2),	796 (0.032),
859 (0.5; w), 909 (0.8),	854 (1; w), 910 (1),	853 (0.033), 912 (0.017),
938 (4), 956 (0.3),	937 (2),	937 (0.047),
970 (1.5), **983 (1.5)**,	980 (2);	979 (0.047),
996 (0.8), **1046 - 1057**(3; w),	1023 (0.5), 1051 (2),	1048 (0.035),
1079 (8), 1095 (2),	1078 (4),	1080 (0.057),
1117 (0.1), **1138 (2)**,	1136 (1),	1136 (0.008),
1162 (0.5), 1170 (0.5),		
1193 (9), 1219 (4)*,	1193 (3),	1195 (0.071), 1220 (0.052),
1248 (4), 1258 (0),	1247 (3),	1252 (0.040),
1270 (1), 1296 (0.5),	1281 (3),	1290 (0.044),
1309 (1), **1348 (3; w)**,	1311 (1), 1353 (2),	1313 (0.041), 1359 (0.052),
1440 (5; w), **1460 (10)**,	1381 (1), 1440 (5),	1452 (0.156),
	1462 (6),	1464 (0.158).

The data presented in Table 3 show that all lines of maximum and medium intensity in the adduced spectra of 1,1,3-trimethylcyclohexane coincide. A few of the lines of low and medium intensity in our 1,1,3-trimethylcyclohexane spectrum are superimposed upon the intense lines of the isomeric hydrocarbons —1,2,3-trimethylcyclohexane [325 (3); 418 (8); 539 (7); 975 (6); 1159 (4); 1193 (4); 1315 (6; w)] [6] and 1,2,4-trimethylcyclohexane [416 (3)] [6]. However, the spectrum we obtained lacked other lines of high intensity typical of 1,2,3-trimethylcyclohexane: 734 (7); 833 (4); 921 (4); 1063 (4); 1233 (3); 1278 (3); 1315 (6; w) [6] and of 1,2,4-trimethylcyclohexane: 455 (3); 522 (3); 615 (5); 747 (8) [6], thus confirming the absence of these isomeric hydrocarbons (the possibility of whose formation was discussed above) in the 1,1,3-trimethylcyclohexane synthesized by us.

Below we present the Raman spectra of two other cyclohexane hydrocarbons we have synthesized — 1,3-dimethyl-1-ethyl cyclohexane and 1,3-dimethyl-1-propylcyclohexane; these spectra were taken under the same conditions as that of 1,1,3-trimethylcyclohexane.

1,3–Dimethyl-1-ethylcyclohexane: 193 (0.1; g), 257 (0.2; w), 276 (0.1; w), 322 (3; w) 345 (2.5), 406 (3), 414 (1), 435 (1), 462 (3), 495 (1.5; db) 518 (0.2), 547 (0), 558 (4), 570 (0.5), 663 (0), 700 (1.5), 722 (4; db), 783 (0), 792 (3; db), 795 (3; db), 846 (1.5), 860 (1.5), 875 (1), 895 (0.5), 943 (0.8), 953 (3), 963 (0.3), 978 (1), 991 (2), 1003 (3), 1023 (0), 1046 (1.2), 1068 (1; db), 1082 (4), 1102 (1), 1107 (0.1), 1141 (2), 1162 (1.5), 1194 (5), 1215 (3), 1227 (2), 1259 (1), 1270 (2.5; w), 1307 (0.5; w), 1347 (1), 1350 (2), 1358 (1), 1382 (0.3), 1439 (10), 1460 (10).

1,3–Dimethyl-1-propylcyclohexane: 274 (1; w), 299 (1.8), 314 (1.5), 336 (0.5), 406 (2), 413 (0.1), 444 (0.3), 467 (1.5), 488 (1.5), 504 (1), 525 (0.8), 567 (2.5), 586 (0.4), 734 (5; w), 746 (0), 769 (0), 796 (2), 820 (0.1), 845 (0), 861 (1.5), 896 (1.2; w) 930 (1), 963 (0.5), 985 (0.5), 1015 (0.5), 1040 (1), 1056 (1.5), 1080 (2), 1105 (1.5), 1133 (1.5), 1165 (1.5), 1190 (.5), 1204 (1.5), 1226 (0.8), 1256 (0.3), 1270 (1), 1294 (1.5), 1310 (1.5), 1354 (0; w); 1388 (0.2), 1440 (9), 1460 (10).

*The line of medium intensity 1219 cm^{-1} discovered in our spectrum but lacking in Chinerdoglu's [6] was also observed by Fenske [7] in the spectrum of this hydrocarbon.

SUMMARY

1.   A new method has been developed for the synthesis of cyclohexane hydrocarbons with two alkyl groups and one carbon atom — 1,3-dimethyl-1-alkylcyclohexenes-2 (alkyl — CH_3, C_2H_5, C_3H_7).   This is a three-stage method;   1) synthesis of 1,3-dimethylcyclohexadiene-1,3;   2) hydrobromination of that compound and 3) reaction of the tertiary allyl hydrobromide thus formed with RMgX.

2.   The structure of the synthesized cyclohexene hydrocarbons was confirmed by their physical properties, including the Raman spectrum of one of them, and also by their stability under irreversible catalysis, which verified the presence of a quaternary carbon atom in the ring.

3.   Hydrogenation of the synthesized hydrocarbons resulted in production of the corresponding cyclohexane hydrocarbons with a quaternary carbon atom — 1,3-dimethyl-1-alkylcyclohexanes.

4.   1,1,3-Trimethylcylcohexene-2,   1,3-dimethyl-1-ethylcyclohexene-2,   1,3-dimethyl-1-propylcyclohexene-2, 1,3-dimethyl-1-ethylcyclohexane and 1,3-dimethyl-1-propylcyclohexane are here described for the first time.

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CATALYTIC ALKYLATION OF BENZENE BY BUTYL ALCOHOL

M. B. Turova-Polyak, N. V. Danilova and E. G. Treshcheva

The butyl benzenes are usually obtained by two methods: the alkylation of benzene by butylene and iso-butylene or the alkylation of benzene by butyl alcohols. These reactions are conducted at atmospheric or elevated pressures, in the liquid phase, in presence of hydrofluoric acid, hydrochloric acid [1,2], boric fluoride [3,4], aluminum chloride [5,6] or other compounds.

In a previous study one of us [7] established the possibility of alkylating benzene with ethyl and propyl alcohols over an aluminum silicate catalyst in a flow system at atmospheric pressure. The present study was the first in which benzene was alkylated by n-butyl alcohol under these conditions. It was established that secondary and n-butyl benzenes are the main reaction products — products of alkylating benzene with butylene. Tertiary butyl benzene is present in the alkylation products only in negligible quantity, and isobutyl benzene is lacking. It follows from this data that isomerization of butylene and isobutylene takes place to only a negligible extent under the conditions of our reaction.

Under optimum conditions, the yield of isomeric butyl benzenes attains 35% of the alcohol used in the reaction.

EXPERIMENTAL

The initial substances used where thiophene-free benzene, b.p. 79.5-80° (755 mm); n_D^{20} 1.5018, d_4^{20} 0.8786 and n-butyl alcohol, b.p. 116-117° (759 mm), n_D^{20} 1.3995, d_4^{20} 0.8095.
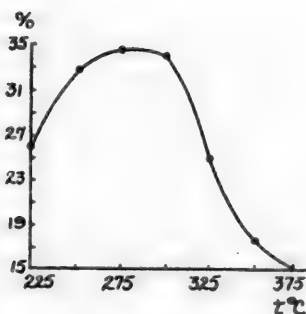
Fig. 1. Butyl benzene yield relative to experiment temperature. Benzene/alcohol ratio is 4 : 1; space velocity 0.66.
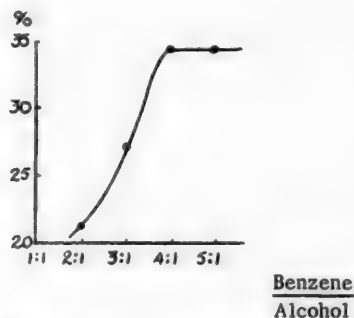
Fig. 2. Butyl benzene yield relative to benzene content of initial mixture.
Temperature 300°; space velocity 0.66.

As in the previous study, the alkylation reaction took place in the vapor phase in a flow system at atmospheric pressure over a commercial aluminum silicate catalyst.

Dependence of butyl benzene yield on temperature (Fig. 1), on composition and rate of delivery of the reaction mixture (Figs. 2-3), and on duration of the experiment (Fig. 4) were investigated.
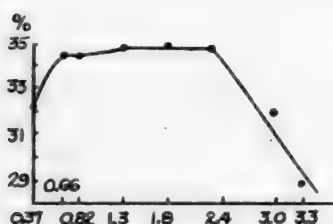
Fig. 3. Butyl benzene yield relative to rate of delivery of reaction mixture.
Benzene/ alcohol ratio is 4 : 1; temperature 300°.
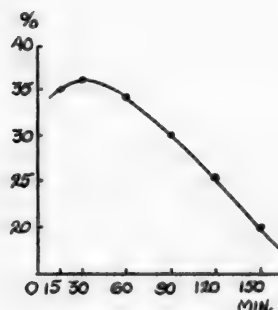
Fig. 4. Butyl benzene yield relative to duration of experiment.
Temperature 300°; benzene/ alcohol ratio is 4 : 1; space velocity 0.66.

These curves show:

1. The optimum temperature of experiment is 275 - 300°. Butyl benzene fraction yield falls steadily with rising temperature.

2. Increasing the benzene content of the reaction mixture to 4 : 1 facilitates a rise in reaction product yield.

3. Butyl benzene fraction yield is virtually constant when the reaction mixture is delivered at a space velocity of between 0.66 and 2.4; further rise in rate of delivery of the mixture brings a reduction in reaction product yield.

4. Butyl benzene fraction yield remains practically constant at durations of experiment between 15 and 60 minutes, but yield falls steadily as duration of experiment increases.

TABLE 1

Fractions	Fraction b.p.	% of fraction in Catalyzate	n_D^{20}
I	32-79°	10.8	1.4630
II	79-85°	63.5	1.4969
III	85-167	4.0	1.4875
IV	167-237	13.5**	1.4895
	losses	8.2	

Catalyzates recovered in the entire series of experiments were of unsaturated type and reacted energetically with permanganate. After the water was driven off, they were dried with calcium chloride and fractionated over metallic sodium. Table 1 presents the results of catalyzates distillation under optimum conditions.

Benzene and n-butyl alcohol were passed separately over catalyst under optimum conditions to discover the reason for the formation of unsaturated compounds in the catalyzates and the origin of the low-boiling fractions (32-79°).

It appeared that the benzene underwent no change under these conditions, but that when the butyl alcohol was so passed, a liquid catalyzate was formed, in quantity 41% of the alcohol used in the reaction, and also gaseous products consisting of unsaturated compounds (89.1%), carbon monoxide (0.6%), hydrogen and saturated compounds (10.3%).

After bromine absorption of the gaseous products, bromides were obtained with constants similar to that of the dibromobutanes.

The liquid portion of the catalyzate was unsaturated in character and reacted actively with a solution of permanganate and bromine water. After distillation of the water it was dried and distilled. Distillation findings are

• The excess benzene was distilled off the 79-85° fraction after processing with concentrated sulfuric acid, and then used in the work.
•• Yield of this fraction relative to initial alcohol was 34.9%.

presented in Table 2.

No more detailed study of the fractions obtained was undertaken. However, the works of Lebedev [8], Kazansky and Rozengardt [9], Maslyansky [10]and others permit us to postulate that the products of the given reaction were formed as the result of polymerization of butylenes.

The Raman spectrum was used to determine the composition of the butyl benzene fraction boiling over the wide range from 167 to 237° (Table 1). The fraction was first treated with concentrated sulfuric acid, appropriately washed, dried and distilled over sodium into finer fractions (Table 3).

T A B L E   2

Fractions	Fraction b.p.	% of fraction in catalyst	n_D^{20}	d_4^{20}	Bromine number	% of unsaturated compounds
I	40°	5.4	1.4036	-	-	-
II	40-70	1.4	-	-	-	-
III	70-100	18.7	1.4040	0.7165	76.5	46.8
IV	100-125	38.6	1.4087	0.7170	82.5	57.7
V	125-150	6.7	1.4210	0.7463	90.7	71.4
VI	150-200•	17.8	1.4540	0.8045	84.8	40.0
	losses	11.6	-	-	-	-

T A B L E   3

Butyl benzene fraction under study	Fraction b.p.	Fraction content (% by weight)	n_D^{20}	d_4^{20}	MR_D	
					found	calculated
I	167-170°	15.0	1.4890	0.8605	44.95	44.77
II	170-172	52.0	1.4896	0.8612	44.91	44.77
III	172-181	5.8	1.4907	0.8631	45.00	44.77
IV	181-183.5	4.8	1.4909	0.8636	45.00	44.77
V	200-237	14.0	1.4925	0.8646	63.80	63.25
losses	-	8.4	-	-	-	-

T A B L E   4

Hydrocarbons	b.p.	n_D^{20}	d_4^{20}
n-Butyl benzene [11]	182-183.1°	1.4880	0.8668
tertiary Butyl benzene	168.5-169.5[14]	1.4919 [15]	0.8665 [15]
secondary Butyl benzene [12]	172.5	1.4898	0.8608
Isobutyl benzene [12]	170.1	1.4928	0.8673
1,4-Di-n-butyl benzene [12]	259 (745 mm)	1.4879	0.8556
1,4-Di-secondary-butyl benzene [12]	237.0	1.4878	0.8573
1,4-Di-tertiary-butyl benzene [12]	237 (m.p.77°)	1.4624 (90°)	0.8659

Comparison of the constants of the individual butyl benzenes (Table 4) with those of the butyl benzene fractions obtained by alkylation of benzene with n-butyl alcohol (Table 3) shows that the alkylation product consisted chiefly of a mixture of isomeric butyl benzenes (77.6%) (Fractions I-IV) with a predominance of secondary butyl benzenes (Fraction II), and of dibutyl benzenes, constituting approximately 14% (Fraction V).

Analysis of Fraction (II), 170-172°.
7.335 mg sub.: 24.105 mg CO_2; 6.930 mg H_2O. 7.305 mg sub.: 24.000 mg CO_2; 6.838 mg H_2O. Found %: C 89.68, 89.66. H 10.57, 10.48. $C_{10}H_{14}$. Calculated %: C 89.52; H 10.51.

All fractions, except that between 200 and 237•, were subjected to Raman spectrum study. The bright lines of all fractions studied fell within a narrow range.

The spectrums of the 167-170° and 170-172° fractions were identical in brightness and frequency of Raman spectrum lines.

Spectra of fractions 167-170° and 170-172°: 229 (1;w); 280 (0.8); 311 (2.5); 333 (3); 461 (7); 546 (0.5); 559(2);

• The small quantity of substance made it impossible to determine the limits of boiling accurately.

588 (1.5); 619 (12); 702 (1); 732 (12); 746 (2.5); 764 (2); 792 (1.5); 808 (2.5); 843 (2); 856 (2.5); 903 (1.5); 929 (0.5); 948 (2.5); 956 (2); 987 (1); 1000 (1.5); 1002 (80); 1034 (25); 1056 (2); 1085-1117 (2; w); 1160 (7); 1189 (6); 1206 (2); 1239 (0.5); 1258 (0.5); 1272 (1.5); 1296 (1); 1323 (0.5); 1335 (1); 1353 (1); 1382 (1); 1397 (1); 1443 (2); 1460 (10); 1584 (4); 1608 (20).

Comparison of the spectra obtained with those for n-butyl benzene, secondary, tertiary and isobutyl benzenes obtained by Genske [13], shows that the fractions studied constituted a mixture of secondary butyl benzene (primarily) with n- and tertiary butyl benzene. The presence of secondary butyl benzene was determined by the brightest lines in the spectrum: 311, 461, 619, **732**, 746, 903, 1002, 1034, 1206.

The presence of n-butyl benzene was established by spectral lines 229, 280, 1056, 1296, while the other n-butyl benzene lines were superimposed upon those of secondary butyl benzene. Tertiary butyl benzene is characterized by spectral lines 702 and 929.

The brightness of the lines of the Raman spectra was not measured photometrically, but visually.

In terms of the data of spectrographic analysis, the content of isomeric butyl benzenes in the fractions under study was approximately the following; secondary butyl benzene 85-90%, n-butyl benzene 10-12%, tertiary butyl benzene — negligible. If isobutyl benzene was present, it could only have been in trace quantity.

The spectrum of the 181-183.5° fraction is very similar to that of the 167-170° fraction. It consists of a mixture of secondary butyl benzene and n-butyl benzene, with a very insignificant admixture of tertiary butyl benzene.

Spectrum of the 181-183.5° fraction: 229 (2); 284 (1.5); 310 (1.8); 333 (1); 405 (0); 462 (2.5; w) 501 (1.5); 565 (1); 598 (1); 612 (10); 701 (0.3); 735 (10); 746 (0.8); 762 (0.8); 792 (0.8); 810 (1.5); 843 (1); 857 (1,5); 904 (2); 948 (2); 956 (0.8); 974 (0.5); 1002 (50); 1034 (20); 1057 (1); 1085 (1.5;); 1117 w); 1157 (5); 1182 (3); 1206 (12); 1241 (0.3); 1286 (1.5; w); 1296 (1.5); 1323 (0.3; g); 1347 (0.5); 1382 (0.3); 1453 (10); 1608 (18).

The presence of secondary butyl benzene was established in terms of lines: 310, 462, 621, 735, 746, 904, 1002, 1034, 1206; and n-butyl benzene by lines: 229, 284, 501, 565, 1057, 1296. Tertiary butyl benzene is characterized by line 701.

The quantitative composition of the fractions was approximately as follows: secondary butyl benzene ~ 75-78%, n-butyl benzene ~ 22-25%, tertiary butyl benzene — traces; isobutyl benzene was lacking.

SUMMARY

1. Alkylation of benzene by n-butyl alcohol in a flow system at atmospheric pressure was performed for the first time.

2. Alkylation resulted in the formation of a mixture of butyl benzenes, with secondary butyl benzene predominating.

3. The optimal conditions for porduction of butyl benzenes must be considered to be a temperature of 300°, and a molar ratio of 4 : 1 between benzene and n-butyl alcohol; a volumetric velocity of delivery of the reaction mixture of 0.66-2.4; under these conditions the butyl benzene yield attains 35% of the alcohol used in the reaction.

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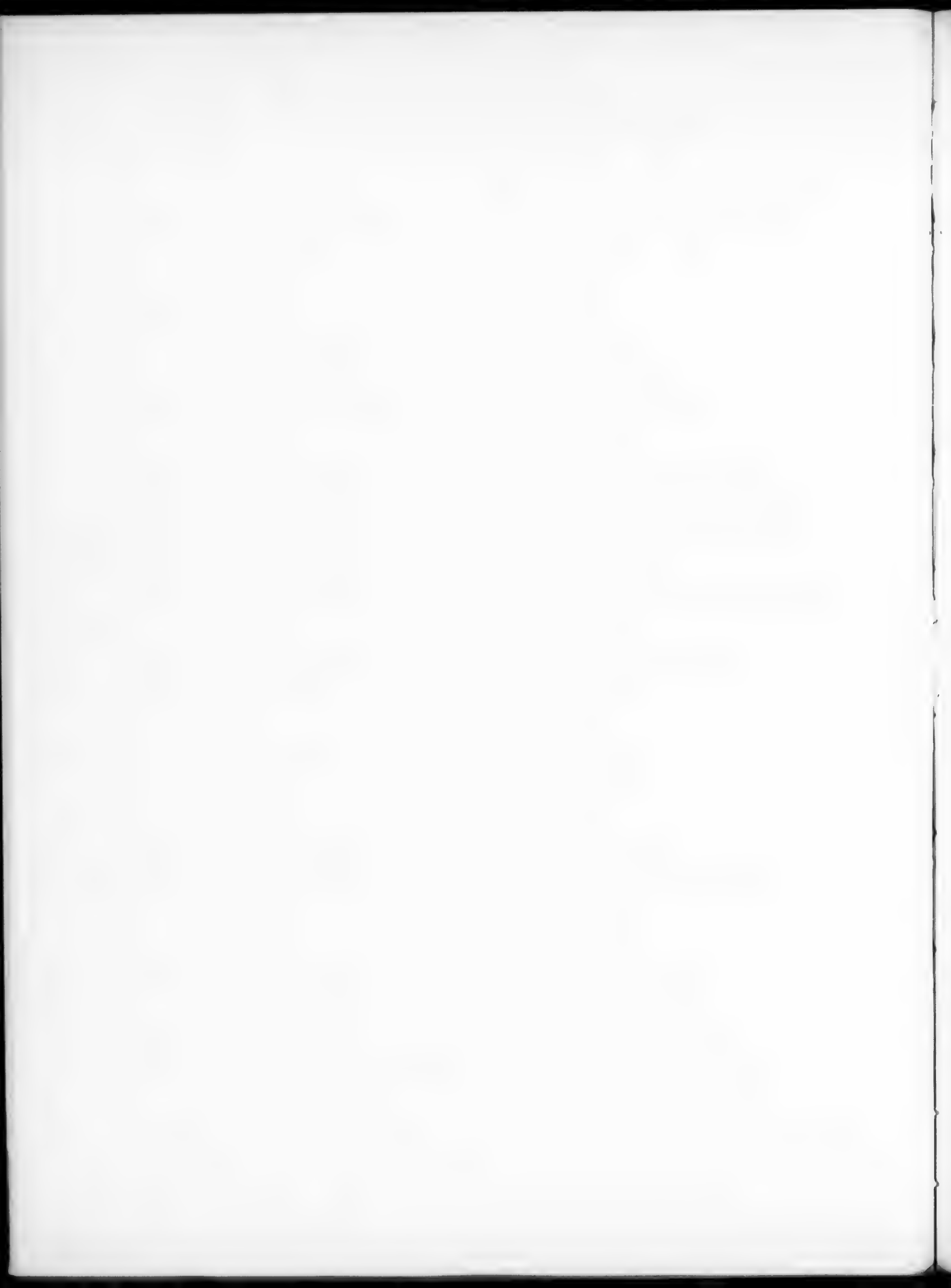
CONTACT CONVERSIONS OF BUTYLCYCLOHEPTANE
IN THE PRESENCE OF PLATINIZED CHARCOAL

S. I. Khromov, E. S. Balenkova and B. A. Kazansky

We have previously shown [1], from study of catalytic conversions of certain alkyl and aryl cycloheptanes over platini zed charcoal under conditions of catalytic dehydrogenation that these hydrocarbons withstand isomerization of the hepta to the hexa cycle with formation of semi-substituted cyclohexane hydrocarbons.

Thus, for example, phenylcycloheptane, the simplest cycloheptane aryl derivative, placed in contact with pla tinized charcoal at 320°, gives about 7% semi-methylphenylcyclohexane; the alkylcycloheptanes (methyl, ethyl- and pr opylcycloheptanes) will yield up to 28% of semi-methylalkylcyclohexanes.

In the development of the previously described cases of isomeric conversion of heptamethylene hydrocarbons it appeared to us to be of interest to study the behavior of butylcycloheptane under conditions of catalytic dehydrogena - tion.With thi s object we synthesized butylcycloheptane, and put this hydrocarbon in contact with 10% platinized charcoal at 320°. The catalyzate (for separation of naphthene hydrocarbons from the aromatics) was subjected to chromatographic adsorption on silica gel. The naphthene portion of catalyzate produced by chromatographic ad- sorption consisted chiefly of 1-methyl-1-butylcyclohexane (semi-methylbutylcyclohexane). The aromatic portion of the catalyst obtained by chromatographic adsorption on silica gel, was distilled in a column of 15 theoretical plates. The composi tion of the separate fractions of the aromatic part of the catalyzate was determined by oxidation with an aqueous solution of potassium permanagate [2].

On the basis of the research results obtained, the approximate proportions of hydrocarbons in the total mass of catalyzate of butylcycloheptane contact conversion, in %, is as follows: about 29% 1-methyl-1-butylcyclohexane; 32% butylbenzene; 25% o-methylbutylbenzene; 6% m-methylbutylbenznee, 4% p-methylbutylbenzene, 3% amylben- zene, and 1% toluene.

The contact conversions of butylcycloheptane may be expressed by the following reaction scheme:
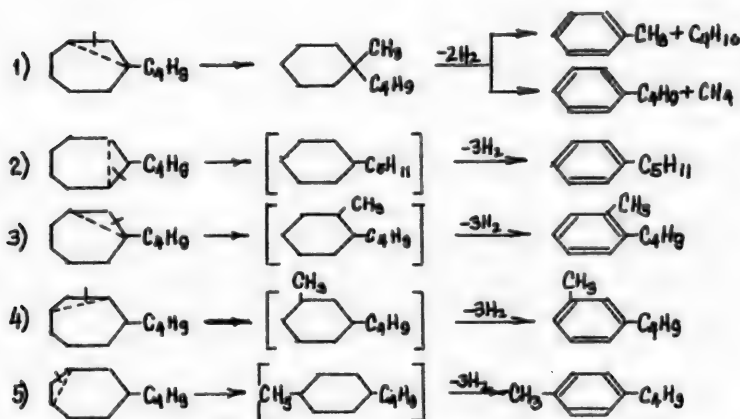
The production of butylbenzene and toluene among the reaction products of catalytic conversion of butylcyclo-heptane is apparently to be ascribed to the occurrence of a secondary process — the catalytic conversion of 1-methyl-1-butylcyclohexane formed in the course of the main reaction. In our experience, as in the cases of catalytic conversion of alkyl and aryl cycloheptanes previously studied, the disruption of the hepta ring during isomerization into hexa ring occurs primarily through a single carbon atom from carbon with alkyl substitutes.

<div align="center">EXPERIMENTAL</div>

Synthesis of butylcycloheptane. 1-Butylcycloheptanol-1 was obtained from suberone and butylmagnesium bro-mide. The alcohol was dehydrated in presence of iodine, and the 1-butylcycloheptene-1 thus formed was hydrogena-ted in presence of platinized charcoal to butylcycloheptane. To eliminate the traces of the unsaturated hydrocarbon the butylcycloheptane was subjected to chromatographic adsorption over silica gel, and then vaccum distilled in a column.

B. p.   80.0° (10mm), 207.4° (755 mm), n_D^{20} 1.4517, d_4^{20} 0.8195; MR_D 50.65. $C_{11}H_{22}$. Calculated. 50.79.

9.629 mg. sub.: 30.249 mg CO_2; 12.315 mg H_2O. 8.170 mg sub.: 25.266 mg CO_2; 10.510 mg H_2O. Found %: C 85.74, 85.72; H 14.30, 14.39. $C_{11}H_{22}$. Calculated %: C 85.63; H 14.37.

Butylcycloheptane is not described in the literature.

Contact conversion of butylcycloheptane. 60 ml of 10% platinized coal was placed in a catalytic tube, and 40 g butylcycloheptane was passed over the catalyst at 320°, with a volumetric velocity of 0.2. The results are shown in Table 1.

T A B L E   1

Pass	n_D^{20}	Gas liberated (ml)	Catalyzate ob-tained, wt (g)
1	1.4728	10360	35.4
2	1.4725	3590	34.2
3	1.4802	1050	33.7
4	1.4816	790	33.4
Total......		15790	-

The gaseous catalysis products were analyzed with a V. T. I. apparatus. The results of gas analysis in %: H_2 86.8; C_nH_{2n+2} 12.7.

Study of the Catalyzate. The catalyzate obtained by con-tact conversions of butylcycloheptane for separation of naph-thene hydrocarbons from the aromatic hydrocarbons formed during catalysis, was subjected to chromatographic adsorpt-ion on silica gel. The naphthene fraction (9.5 g) evolved by this method of dissociation boiled at 191-191.5° (763 mm), n_D^{20} 1.4477, d_4^{20} 0.8129, MR_D 50.63. $C_{11}H_{22}$. Calc. 50.79.

The constants of the 1-methyl-1-butylcyclohexane previously synthesized by us were [3]: b.p. 191.5° (758 mm), n_D^{20} 1.4477, d 0.8137.

To confirm the presence of 1-methyl-1-butylcyclohexane in the catalysis products, the naphthene portion of the catalyst was also studied by the Raman spectrum method. Comparison of the spectrum of the naphthene portion of the butylcycloheptane catalyzate studied with that of pure 1-methyl-1-butylcyclohexane demonstrated their identity.

The aromatic portion of the catalyzate (23.4 g) was subjected to fractionation in a column. Table 2 presents the results of this distillation.

Distillation of the residue in a small retort gave a fifth fraction, 9.4 g in quantity, boiling at 195-203° (751 mm), n_D^{20} 1.4990, d_4^{20} 0.8742.

T A B L E   2

Fraction No.	Boiling range at 751 mm	n_D^{20}	d_4^{20}	Weight (g)	Weight , %
1	110-114°	1.4961	-	0.3	1.3
2	114-182	1.4899	0.8609	0.8	3.4
3	182-185	1.4901	0.8618	8.9	38.0
4	185-195	1.4926	0.8692	2.6	11.1
	Residue	-	-	9.7	41.5
	Losses	-	-	1.1	4.7

The first fraction, as indicated by its constants, consisted chiefly of toluene. Nitration of this fraction gave a ni-tro product which, upon recrystallization from ethanol, showed an m.p. of 69-70°. A sample mixed with pure 2,4-di-nitrotoluene melted at the same temperature.

The second fraction was not studied, in view of its broad boiling range and small quantity.

3rd Fraction. 2.5 g of the third fraction was oxidized by an aqueous potassium permanganate solution. Oxidation gave 2.12 g benzoic acid, m.p. 120.5°.

Comparison of the third fraction constants with those in the literature on butylbenzene made it possible to conclude that it consisted chiefly of that compound.

Data on butylbenzene in the literature [4]: b.p. 183.35 (760 mm), n_D^{20} 1.4897, d_4^{20} 0.8608.

The fact that oxidation of the third fraction gave only benzoic acid completely confirmed the fact that the fraction consisted solely of butylbenzene.

4th Fraction. Oxidation of 2.6 g of this fraction gave the following acids: benzoic (0.12 g), orthophthalic (0.33 g), isophthalic (0.45 g) and terephthalic (0.38 g).

5th Fraction. Oxidation of 6.0 g of the fifth fraction revealed the following acids: benzoic (0.30 g), orthophthalic (2.29 g), isophthalic (0.32) and terephthalic (0.15 g).

The presence of benzoic acid in the oxidation products of the 5th fraction (and partially of the 4th) is to be ascribed to the oxidation of amylbenzene, and not butylbenzene, as the boiling point of the latter is considerably below the distillation range of the fifth fraction. Formation of phthalic acids in the 4th and 5th fractions must be ascribed to oxidation of the o-, m- and p-methylbutylbenzenes.

Table 3 presents a typical composition of the aromatic portion of butylcycloheptane catalyst, computed in terms of chemical analysis and the physical constants of the fractions obtained.

T A B L E   3

Fraction No.	Boiling range, 751 mm	Weight (g)	% of total aromatic hydrocarbons	percentage content of					
				toluene	butyl-benzene	methylbutylbenzenes			amyl-benzene
						ortho	meta	para	
1	110-114°	0.3	1.3	1.3	-	-	-	-	-
2	114-182	0.8	3.6	-	3.6	-	-	-	-
3	182-185	8.9	40.4	-	40.4	-	-	-	-
4	185-195	2.6	11.9	-	1.0	2.9	4.0	3.5	0.5
5	195-203	9.4	42.8	-	-	32.6	4.4	2.1	3.7
	Total....	22.0	100.0	1.3	45.0	35.5	8.4	5.6	4.2

SUMMARY

1. n-Butylcycloheptane was synthesized and described for the first time.

2. The contact conversions of butylcycloheptane in presence of platinized charcoal at 320° were studied, and it was established that they result in the formation of considerable quantities of 1-methyl-1-butylcyclohexane and mixtures of aromatic hydrocarbons consisting of toluene, butylbenzene, o-, m- and p-methylbutylbenzenes.

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BROMINATION OF 1,1-DIPHENYLETHANE

I. P. Tsukervanik and K. Yu. Yuldashev

Continuing the study of the halogenation of 1,1-diphenylethane undertaken by one of us [1], we investigated its bromination reaction. This reaction was been described by Scheibly and Prutton [2]. These authors reacted 1,1-diphenylethane with various quantities of bromine in the light, at 100°. A very insignificant quantity of stilbene was separated out upon distillation of the reaction mixture and, in another case, some 1,1,4,4-tetraphenylbutadiene-1,3. The main bromination product was an oil which these authors did not study at all.

We brominated 1,1-diphenylethane, produced from acetylene and benzene [3] in a quartz flask lit by an electric bulb, at 100 to 200°. Gradual addition of bromine resulted in an energetic reaction with heavy production of hydrogen bromide. The products were separated by distillation, followed by crystallization.

The results varied with the bromine consumption. When 1.3 mole of bromine was used per 1 mole of 1,1-diphenylethane, the product was 1,1-diphenylethylene (I) with a yield of 70% of the theoretical, plus a small amount (12%) of 1,1-diphenyl-2-bromethylene (II).

When 2 mole of bromine was used, the result was a readily crystallized oil, from which the following were obtained: (II) (63%) and 1,1,-diphenyl-2-2-dibromethylene (III) (12%). The latter was the sole product when 3 mole of bromine was used; it was obtained in a yield of 84% of the theoretical.

Identification of (III) was performed by means of the ′Goldschmidt reversible reaction [4]. Identification of (II) was by conversion to tolane by fusion with an alkali [5]. Further, (II) was synthesized from 1,1-diphenylethylene [5].

Thus, the following products may be obtained from 1,1-diphenylethane, depending upon the quantity of bromine:

$$(C_6H_5)_2CHCH_3 \rightarrow (C_6H_5)_2CBrCH_3 \rightarrow (C_6H_5)_2CBrCH_2Br \rightarrow (C_6H_5)_2CBrCHBr_2$$
$$\downarrow -HBr \qquad \downarrow -HBr \qquad \downarrow -HBr$$
$$(C_6H_5)_2C=CH_2 \qquad (C_6H_5)_2C=CHBr \qquad (C_6H_5)_2C=CBr_2.$$
$$\text{(I)} \qquad\qquad \text{(II)} \qquad\qquad \text{(III)}$$
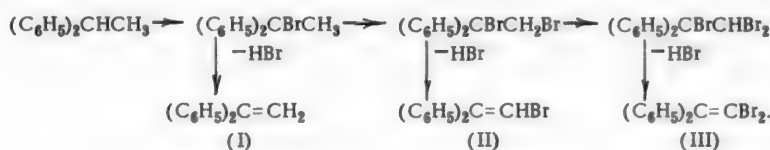
It is apparent that the reactions proceed by the substitution of one, two or three of the ethane hydrogens by bromine, and the subsequent liberation of hydrogen bromide. We made repeated attempts to isolate the primary products. With this object, the reaction was performed at the lowest possible temperatures (30-80°), and the raw mixture was not subjected to distillation. Crystallization of the resultant oil was not successful in a single instance. These oils probably consist of a mixture of saturated and unsaturated bromides.

Our results differ sharply from those obtained by Scheibly and Prutton [2]. We attempted in several experiments, in which we adhered to all the conditions set forth by these authors, to obtain 1,1,4,4-tetraphenylbutadiene-1,3. Invariably, however, the results of bromination failed to differ from those adduced above. It is possible that this discrepancy may be explained by the inadequate purity of the 1,1-diphenylethane employed by Scheibly and Prutton.

EXPERIMENTAL

1,1-Diphenylethylene (I). 20 g (0.11 mole) 1,1-diphenylethane (b.p. 265-270° at 730 mm) was placed in an open quartz flask illuminated by a 500-watt lamp. A thermometer and the bottom of a dropping funnel from which the bromine was delivered were placed in the above liquid. 7 ml (0.14 mole) bromine was added in the course of an hour, the temperature of the mixture being maintained within the range of 160-200°. 19.3 g of the raw product, showing a b.p. of 270-310°, was obtained. Repeated distillation in a vacuum gave 14 g (about 70%) 1,1-diphenylethylene, b.p. 140-143° (6 mm), and 3.4 g 1,1-diphenyl-2-bromoethylene (II), b.p. 160-170° (6 mm).

To remove the bromine residue, the 1,1-dephenylethylene was agitated with molecular silver and fractionated over sodium. The isolated pure product showed constants in complete correspondence with the data presented in the literature [6]:

B.p. 133.0° (6 mm), d_4^{20} 1.0260, n_D^{20} 1.6014, MR_D 60.22; calc. 59.30.

Bromination in a chloroform solution gave 1,1-diphenyl-2-bromethylene (II) with m.p. 40° [5].

1,1-Diphenyl-2-bromoethylene (II). 14 ml (0.28 mole) bromine was added in the course of an hour to 20 g 1,1-diphenylethylene. 24 g oil, b.p. 290-325°, was liberated. The oil crystallized upon cooling. It gave 4.5 g (12%) 1,1-diphenyl-2,2-dibromethylene, m.p. 83° (from alcohol). After repeated distillation, the remaining oil gave pure 1,1-diphenyl-2-bromoethylene (II), m.p. 40°. The yield was 18 g (63%).

1 g 1,1-diphenyl-2-bromoethylene was fused with 2 g caustic potash [5]. This gave 0.6 g (90%) tolane, m.p. 60°.

1,1-Diphenyl-2,2-dibromethylene (III). As described above, 10 g (0.06 mole) 1,1-diphenylethane was brominated with 10 ml bromine (0.19 mole). This gave 15 g (83.5%) of a completely crystallizing product. Recrystallization from alcohol resulted in isolation of pure 1,1-diphenyl-2,2-dibromethylene (III), m.p. 83-83.5°. An attempt to mix it with the synthesized product by the accepted method [4] did not result in depressing the m.p. Oxidation of the chromium anhydride produced benzophenone, m.p. 47-48°, while its semicarbazone had an m.p. of 166°.

SUMMARY

1. Bromination of 1,1-diphenylethane under light proceeds, with elevation of temperature, to substitution of ethane hydrogens and subsequent liberation of hydrogen bromide

2. Depending upon the quantity of bromine used, the following products are readily produced, with good yields: 1,1-diphenylethylene, 1,1-diphenyl-2-bromethylene and 1,1-diphenyl-2,2-dibromethylene.

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ACYLHYDROXYSILANES IN THE SYNTHESIS OF

KETO ACIDS OF THE AROMATIC SERIES

Yu. K. Yuryev, G. B. Elyakov and Z. B. Belyakova

Keto acids of the aromatic series have been adequately studied. Of the numerous existing methods for their synthesis we might single out the Gustavson-Friedel-Crafts reaction, where the anhydrides or chloroanhydrides of dibasic acids are used as the acylating agent. The latter, however, are not so convenient since reaction with them proceeds in two directions, and the corresponding diketone results in addition to the keto acid.

By acylation of benzene with succinic anhydride, β-benzoylpropionic acid [1,2,3] was obtained, by acylation with phthalic anhydride, o-benzoylbenzoic acid [4,5] resulted; by acylation with glutaric and sebacic acid chloroanhydrides, Auger [6], and later Borsche and Wollemann [7,8] obtained γ-benzoylbutyric acid and θ-benzoylpelargonic acid, respectively.

Among other synthetic methods for aromatic keto acids can be indicated, for example, the reaction of dibasic acid anhydrides with organomagnesium compounds [9]. This reaction does not proceed in a well-defined manner, and side products are obtained in addition to the keto acid.

Ketone split of the corresponding α-benzoylsubstituted ester of dibasic acids can also serve as a synthetic method for aromatic keto acids [10,11].

Of particular interest are the first members of the aromatic keto acid series — benzoylformic and benzoylacetic acids, as well as their esters. Benzoylformic acid can be obtained by hydrolysis of benzoyl cyanide [12], as well as by oxidation of acetophenone [13], or amygdalic acid [14]. Beckman and Paul [15] obtained benzoylacetic acid by reacting carbon dioxide with the sodium derivative of acetophenone. A simpler procedure for obtaining the latter is through hydrolysis of the benzoylacetoethyl ester [16]. The latter can be obtained according to the method of Gustavson-Friedel-Crafts, using the chloroanhydride of malonic acid, the ethylester of the acid [17], or in better yields according to the Claisen reaction [18,19], from benzoyl chloride and ethyl acetate in the presence of sodium ethylate.

In the present work, the authors propose a new method for synthesis of keto acids of the aromatic series, using only the free dibasic acid, not its anhydride or chloroanhydride, and obtaining good results.

It is known that during reaction of silicon tetrachloride with monobasic acids reactive compounds are formed — the tetraacylhydroxysilanes [20], which can be used as acylating agents for the synthesis of aromatic [20] and heterocyclic ketones [21].

Acylation of benzene with tetraacylhydroxysilanes of the dibasic acids in the presence of aluminum chloride has not been studied. The authors have established that with a similar acylation of benzene, reaction proceeds in a well-defined manner and leads to the corresponding aromatic keto acid. The reaction mechanism, as well as the structure of the intermediate reaction product — the acylhydroxysilane of the dibasic acid — requires further study.

$(n = 2,3,4,8)$;
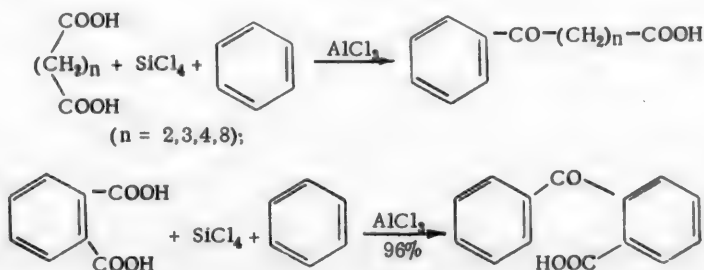
By such means the authors obtained in good yields β-benzoylpropionic, γ-benzoylbutyric, δ-benzoylvaleric, θ-benzoylpelargonic and o-benzoylbenzoic acids.

It should be mentioned that no positive results were obtained with oxalic acid. On introduction of malonic acid into the reactions, acetophenone resulted; upon acylation with ethyl malonate, the benzoylacetoethyl ester was obtained, and along with it, ethylbenzene.

EXPERIMENTAL

Working Procedure. 0.05-0.1 mole of dibasic acid, 500 ml of dry benzene and 0.09 mole of silicon tetrachloride were introduced into three-necked flask equipped with mechanical stirrer and reflux condenser protected from moisture by a calcium chloride tube. The reaction mixture was heated on a water bath first at 60-80°, and then on a boiling water bath with vigorous stirring to complete cessation of hydrogen chloride evolution.

0.15 mole of anhydrous aluminum chloride was introduced by portions into the pre-cooled mixture with stirring. There was no noticeable reaction in the cold, but with heating on a water bath at 60-70° (thermometer in bath) evolution of hydrogen chloride began, and the reaction mixture became brown or brown-gray in color. Reaction was carried out to completion, heating 2-3 hours on a boiling bath, the reaction flask then cooled with ice, and decomposed with ice water, color usually disappearing, evidently due to decomposition of the complex. Excess benzene was distilled off with water vapor, and the residue transferred to a beaker and acidified with concentrated hydrochloric acid with ice cooling. The precipitate was separated, washed with ice water, transferred to a beaker with a solution composed of 50 g of sodium carbonate in 150 ml of water, and boiled for 10-15 minutes. The hot solution was filtered (if colored it was treated with charcoal) and the keto acid isolated from the filtrate by acidification with concentrated hydrochloric acid.

The keto acids which resulted were usually sufficiently pure; they were recrystallized from water or dilute alcohol.

β-Benzoylpropionic Acid. 11.8 g of succinic acid, 10 ml of silicon tetrachloride and 20 g of aluminum chloride in 500 ml of dry benzene. 9 g (51%) of keto acid resulted with m.p. 114-155°. After recrystallization from water, the β-benzoylpropionic acid melted at 116°.

Found %: C 67.81, 67.88; H 5.86, 5.73. $C_{10}H_{10}O_3$. Calculated %: C 67.39; H 5.65.

Literature data: m.p. 116.5° [3].

γ-Benzoylbutyric Acid. 6 g of glutaric acid, 8 ml of silicon tetrachloride and 10 g of aluminum chloride in 309 ml of dry benzene. 5 g (57.5%) keto acid resulted with m.p. 124-125°. After recrystallization from water, the γ-benzoylbutyric acid melted at 126-127°.

Found %: C 69.14, 69.20; H 6.35, 6.34. $C_{11}H_{12}O_3$. Calculated %: C 68.74; H 6.29.

Literature data: m.p. 125-126 [6].

δ-Benzoylvaleric Acid. 14.6 g of adipic acid, 10 ml of silicon tetrachloride and 20 g of aluminum chloride in 500 ml of dry benzene. 13.6 g (68%) of keto acid resulted, with m.p. 73.74°. After recrystallization from water, δ-benzoylvaleric acid melted at 77°.

Found %: C 70.28, 70.20; H 6.91, 6.93. $C_{12}H_{14}O_3$. Calculated %: C 69.87; H 6.84.

Literature data: m.p. 72-73° [3]; 77-78° [22].

θ-Benzoylpelargonic Acid. 10.1 g of sebacic acid, 10 ml of silicon tetrachloride and 20 g of aluminum chloride in 500 ml of dry benzene. 10.5 g (80%) of keto acid resulted with m.p. 75-78°. After recrystallization from dilute alcohol, the θ-benzoylpelargonic acid melted at 82°.

Found %: C 73.37, 73.41; H 8.65, 8.60. $C_{16}H_{22}O_3$. Calculated %: C 73.26; H 8.45.

Literature data: m.p. 77-79° [6], 85-86° [7].

2-Benzoylbenzoic Acid. 8.3 g of phthalic acid, 10 ml of silicon tetrachloride and 20 g of aluminum chloride in 500 ml of dry benzene. 11.8 g (96%) of keto acid resulted with m.p. 91-92°. The keto acid was in the form of a crystalline hydrate with 1 molecule of water. Anhydrous 2-benzoylbenzoic acid with m.p. 127° resulted after recrystallization from xylene.

Found %: C 74.21, 74.26; H 4.62, 4.59. $C_{14}H_{10}O_3$. Calculated %: C74.31; H 4.45.

Literature data: m.p. of the crystalline hydrate was 93-94° [23-24], m.p. of the anhydrous keto acid was 127° [23].

Benzoylethyl Acetate. Obtained by use of milder conditions for the reaction and separation. The silico-anhydride was obtained in similar fashion as described for monobasic acids [21] — from 9 g of freshly-distilled ethyl malonate and 6 g of silicon tetrachloride in 200 ml of anhydrous benzene. 10 g of aluminum chloride was added in portions over a half-hour (the complex forming was red in color). It was heated on a water bath for 4 hours; bath temperature should not exceed 80°. After decomposition with ice water, the reaction mixture was filtered, the benzene layer separated, washed with 2 N sulfuric acid [17], and then washed with water. The aqueous solution was extracted with ether. The benzene-ether extracts were dried with anhydrous magnesium sulfate, and the solvents then distilled off in vacuo and the residue then fractionated.

4.3 g (33%) of benzoylethyl acetate resulted:

B. p. 148-150° (12 mm), n_D^{20} 1.5145, d_4^{20} 1.114. MR_D 52.02. $C_{11}H_{12}O_3$. Calc. 52.10.

Found %: C 68.32, 68.29; H 6.45, 6.39. $C_{11}H_{12}O_3$. Calculated %: C 68.74; H 6.29.

The compound gave an intense red-violet coloration with iron.

Literature data: b.p. 132-137° (4 mm), 165-169° (20 mm) [19]; 159-165° (18 mm) [18].

In addition to the benzoylacetic ester, ethyl benzene was also isolated from the reaction product in the amount of 2.2 g , having the following constants: b.p. 135° (745 mm), n_D^{20} 1.4961, d_4^{20} 0.868.

Acetophenone. Obtained in 44% yield of theory from 10.4 g of malonic acid, 10 ml of silicon tetrachloride and 20 g of aluminum chloride in 500 ml of dry benzene. The b.p. was 200-204°; n_D^{20} 1.5345, d_4^{20} 1.036.

SUMMARY

1. A new synthetic method is proposed for aromatic keto acids — the acylation of benzene with the silico-anhydrides of dibasic acids — which permits use of the dibasic acids themselves in the reaction.

2. By such method the following have been prepared: β-benzoylpropionic, γ-benzoylbutyric, δ-benzoyl-valeric, θ-benzoylpelargonic and 2-benzoylbenzoic acids.

3. From the example of benzoylethyl acetate preparation, the possibility for acylation of the benzene ring with the aid of dibasic acid esters has been demonstrated.

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BARBITURIC ACIDS

II. SYNTHESIS OF METHYLENE-BIS-5-ALKENYLBARBITURIC ACIDS

R. Ya. Levina and N. N. Godovikov

In a previous communication [1] the synthesis of methylene-bis-5-alkylbarbituric acids from methylene-bis-alkylmalonic esters was described. It was established that alkylation of methylene-bis-malonic ester by halide alkyls (in the synthesis of the methylene-bis-alkylmalonic esters) is accompanied by partial dissociation of the intermediate reaction product — the sodium derivative of the monoalkylated methylene-bis-malonic ester — with the formation of methylenemalonic (I) and sodium alkylmalonic (II) esters.

This side reaction proceeds at a yield of 11 to 32% of the theoretical, when primary halides of normal structure ($RX = CH_3Br$, C_2H_5Br, C_3H_7Br and C_4H_9Br) are used, and at 58-61% for primary halides of the iso structure (RX = iso-C_4H_9Br; iso-$C_5H_{11}Br$).

When benzyl chloride is used, the sodium benzylmalonic ester (II) formed reacts further with benzyl chloride to form dibenzylmalonic ester.

The present work studied the substitution reaction of displaceable a-carbons by unsaturated allyl-type radicals in methylene-bis-malonic ester.

When allyl chloride was reacted with methylene-bis-sodium malonic ester, the normal reaction product was obtained at a yield of 30.6% of the theoretical, while the reaction side product (diallylmalonic ester) was obtained at a yield of 58.7%. When the primary unsaturated chloride of branched structure, methallylchloride, was used, the side reaction went even further (87.2%), similarly to what had occurred with the primary alkyl halides of iso-structure; the main reaction product was dimethallylmalonic ester; methylene-bis-methallylmalonic ester was obtained at a yield of only 5% of the theoretical.

(R = allyl and methallyl)
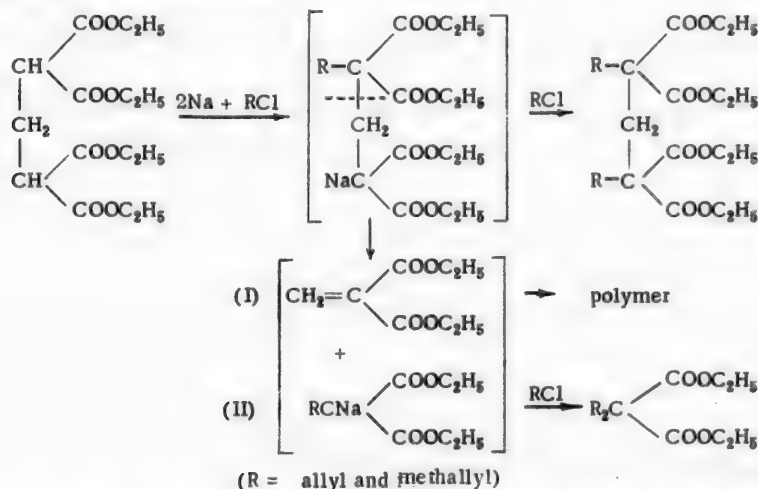
Thus, while use of alkyl halides in reaction with methylene-bis-malonic ester [1] results in monoalkylated malonic ester cleavage products, when primary unsaturated allyl-type halides with a displaceable halide atom (benzyl-, allyl- and methallylchlorides) are brought into the reaction, this side reaction results in the formation of disubstituted malonic esters.

Diallyl- and dimethallylmalonic esters were also directly synthesized from malonic ester. In order to identify these esters, obtained during reaction by cleavage from methylene-bis-malonic ester, they were hydrolyzed into their homologous acids: sample mixtures of these acids with known diallyl- and, correspondingly, dimethallylmalonic acid gave no depression upon melting.

It is necessary to note that an attempt to obtain disecondary pentenylmalonic ester by action of piperylene hydrochloride (a secondary chloride of the allyl type) upon sodium malonic ester under the same conditions which permitted ready synthesis of diallyl- and dimethallylmalonic esters gave, as reaction product, mono-secondary pentenylmalonic ester (penten-2-yl-malonic ester):

$$CH_2 \begin{array}{l} COOC_2H_5 \\ \\ COOC_2H_5 \end{array} \xrightarrow{2Na\ +\ 2CH_2-CH=CH-CHCl} CH_3-CH=CH-CH-\overset{\overset{\displaystyle CH_3}{|}}{CH} \begin{array}{l} COOC_2H_5 \\ \\ COOC_2H_5 \end{array}$$
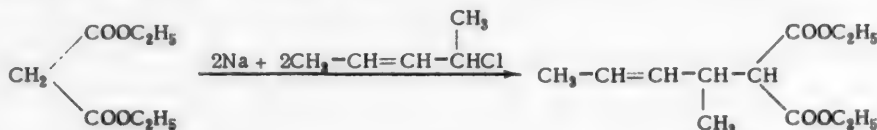
The synthesized methylene-bis-allyl and methylene-bis methallylmalonic esters were converted by action of urea in presence of sodium ethylate into the homologous methylene-bis-5-alkenylbarbituric acids:

$$\begin{array}{c} C_2H_5OOC \\ \\ C_2H_5OOC \end{array} \overset{\displaystyle C-CH_2-C}{\underset{R\qquad\quad R}{|}} \begin{array}{c} COOC_2H_5 \\ \\ COOC_2H_5 \end{array} \xrightarrow[(C_2H_5ONa)]{2CO(NH_2)_2} Na$$

$$\longrightarrow CO \begin{array}{l} NH-CO \\ \\ NH-CO \end{array} \overset{\displaystyle C-CH_2-C}{\underset{R\qquad\quad R}{|}} \begin{array}{l} CO-NH \\ \\ CO-NH \end{array} CO$$

[R = allyl (III) and methallyl (IV)].
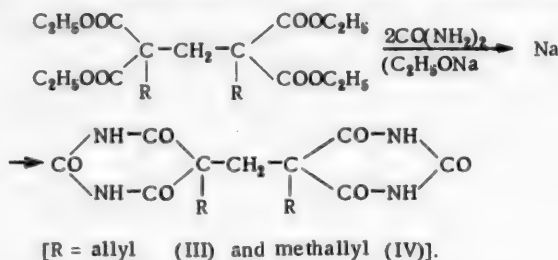
The secondary pentenylmalonic ester also gave the homologous 5-alkenylbarbituric acid (V):

$$CH_3-CH=CH-CH-\overset{\overset{\displaystyle CH_3}{|}}{CH} \begin{array}{l} CO-NH \\ \\ CO-NH \end{array} CO$$

(V)
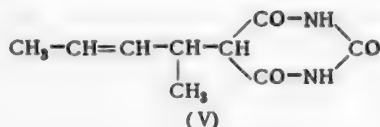
EXPERIMENTAL

Alkylation of methylene-bis-malonic ester (b.p. 174-177°, 5 mm, n_D^{20} 1.4425) and production of the barbituric acids followed the procedure described in our previous communication [1].

1. Methylene-bis-allylmalonic ester. Three fractions were obtained from the reaction product of methylene-bis-sodium malonic ester (0.1 mole) and allyl chloride (0.3 mole) upon fractional distillation:

1st fraction [14 g (58%); b.p. 120-122° at 12 mm, n_D^{20} 1.4468], judging by its constants, constituted diallyl-malonic ester; (data in the literature [2]: b.p. 243-244°; $n_D^{15.3}$ 1.4477); it was identified by conversion into diallyl-malonic acid• with m.p. 132-133° upon recrystallization from benzene (data from literature [3]: m.p. 132-133°). A sample mixture with specially synthesized diallyl malonic acid gave no depression.

The 2nd fraction (2.5 g; b.p. 130-180° at 12 mm) gave, after standing and the addition of a few drops of ether, 1.9 g (11.1%) of a polymer of methylenemalonic ester, m.p. 154-155°. The data in the literature [4] are m.p. 154-156°.

The third fraction (12.6 g; b.p. 201-203° at 10 mm) crystallized completely upon addition of dilute alcohol and cooling with dry ice. The methylene-bis-allylmalonic ester (yield 30.6%) thus obtained, melted at 30-31°, after recrystallization from dilute alcohol. According to the literature [5]: m.p. is 30-31°.

• Hydrolysis consisted of heating 1 g ester with an alcohol potassium chloride solution for 1.5 hr. The precipitated potassium salt, not dissolved in the alcohol, was air dried and, upon addition of dilute hydrochloric acid, gave 0.45 g (69%) diallylmalonic acid.

2. Methylene-bis-methallylmalonic ester. After fractional distillation, the reaction product of methylene-bis-sodium malonic ester (0.1 mole) and methallyl chloride (0.3 mole), gave the following 3 fractions:

The 1st fraction [23 g (85%); b.p. 115-116° and 5 mm, n_D^{20} 1.4537] judging by its constants, consisted of dimethylmalonic ester; (data in the literature [6]: b.p. 114-116° at 1 mm, n_D^{25} 1.4532); it was hydrolyzed as described above into dimethallylmalonic acid, m.p. 176-177°, after recrystallization from bnezene (yield 50%, not described in the literature). A sample mixed with specially synthesized dimethallylmalonic acid melted without depression.

8.320 mg sub.: 19.053 mg CO_2; 5.695 mg H_2O. 7.145 mg sub.: 16.393 mg CO_2; 4.870 mg H_2O. Found %: C 62.44, 62.39; H 7.64, 7.65. $C_{11}H_{16}O_4$. Calculated %: C 62.26; H 7.59.

The second fraction (4.7 g; b.p. 160-173° at 5 mm), upon addition of ether, gave 3.5 g (20%) of a polymer of methylenemalonic ester (m.p. 155-156°).

The third fraction (6.7 g; b.p. 203-207° at 7 mm), upon addition of dilute alcohol and cooling with dry ice gave 2.5 g (5%) methylene-bis-methallylmalonic ester, m.p. 44-45° (upon recrystallization from dilute alcohol).

6.650 mg sub.: 15.235 mg CO_2; 5.000 mg H_2O. 3.770 mg sub.: 8.650 mg CO_2; 2.850 mg H_2O. Found %: C 62.52, 62.61; H 8.41, 8.46. $C_{23}H_{36}O_8$. Calculated %: C 62.67; H 8.24.

Methylene bis-methallylmalonic ester is not described in the literature.

3. Secondary pentenylmalonic ester. Reaction of piperylene hydrochloride* (0.5 mole) with sodium malonic ester (0.25 mole) took place under the normal conditions for obtaining dialkylmalonic esters. However, the main reaction product proved to be monosubstituted** malonic ester (secondary pentenylmalonic):

B. p. 115-117° (9 mm), n_D^{20} 1.4402, d_4^{20} 0.9919, MR_D 60.61. Calc. 60.46. Yield was 57% of the theoretical.

6.405 mg sub.: 14.920 mg CO_2; 5.160 mg H_2O. 8.620 mg sub.: 20.040 mg CO_2, 6.910 mg H_2O. Found %: C 63.57, 63.44; H 9.01, 8.97. $C_{12}H_{20}O_4$. Calculated %: C 63.13; H 8.80.

Secondary pentenylmalonic ester is not described in the literature.

4. Barbituric acids. The barbituric acids were obtained by reacting methylene-bis-alkenylmalonic esters, and also secondary pentenylmalonic ester, with urea in the presence of sodium ethylate, in the usual way [1].

The constants and the analytical data for the barbiturates obtained are presented in the table.

Barbituric Acids

Name	Formula	M.p.	% yield	N (in %)	
				found	calculated
Methylene-bis-5-allylbarbituric acid	III	267-268° (decomposed)	52.6	15.85 15.90	16.09
Methylene-bis-5-methallylbarbituric acid	IV	298-299 (decomposed)	40.0	14.55 14.48	14.88
5-Secondary-pentenylbarbituric acid	V	147-148	98.0	14.99 14.94	15.20

SUMMARY

1. A study was made of the reactions between methylene-bis-sodium malonic esters and the primary unsaturated chlorides — allyl chlorides and methallyl chloride.

2. It was determined that the alkenylhalides of allyl type behave like the alkylhalides in this reaction: when the primary chloride of normal structure is used — the allyl chloride — the yield of methylene-bis-allylmalonic ester attains 30.6%, while when the primary chloride of branched structure — methallylchloride— is used, the yield of methylene-bis-methallylmalonic ester is only 5% of the theoretical.

* Piperylene hydrochloride was obtained by saturating piperylene with gaseous hydrogen chloride, with cooling. The hydrochloride thus obtained was reacted without prior distillation.
** Diallyl- and dimethallylmalonic esters were obtained under the same conditions and with the same reagent proportions, in 71 and 55 % of theoretical yield, respectively.

3. It was shown that when allylation of methylene-bis-malonic ester occurs, the same side-reaction takes place as when it is alkylated — there is a cleavage of an intermediate product, monoalkenyl-methylene-bis-malonic ester, under the influence of sodium ethylate, into methylene-malonic ester (which later converts to the crystalline polymer) and monoalkenylmalonic ester; the latter reacts further readily with allyl halides, resulting in the formation of di-alkenylmalonic ester. This side reaction occurs to a greater degree when the chloride of branched structure is used, and the yields of diallyl- and dimethallylmalonic esters constitute, respectively, 58 and 87% of the theoretical.

4. The following acids were obtained that are not described in the literature: methylene-bis-5-allylbarbituric, methylene-bis-5-methallylbarbituric and 5-secondary-pentenylbarbituric.

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SYNTHESIS OF ALKOXYETHYLIDENELACTAMS

I. ALKOXYETHYLIDENECAPROLACTAMS

M. F. Shostakovsky and F. P. Sidelkovskaya

Alkoxyethylidenelactams are of considerable interest in that they belong to the group of compounds simultaneously containing nitrogen and oxygen with a single carbon atom.

This research resulted in the production and description of alkoxyethylidenecaprolactams. A number of reactions were investigated with their production in mind: reaction of a-chloroethylalkyl ethers with caprolactams, addition of caprolactam to vinylalkyl ethers, and addition of alcohols to vinylcaprolactam.

We obtained our best results by the first method, i.e., by reacting a-chloroethylalkyl ethers with caprolactam. The reaction is exceptionally easy to obtain and proceeds at room temperature. Slight elevation of temperature speeds the process (50-60°) and facilitates improved yield. The reaction was studied in greatest detail when a-chloroethyl butyl ether was used. It is important to state that the yield of products depends heavily on the ratio of the initial materials. With a 1 : 1 ratio the reaction products are caprolactam hydrochloride, butoxyethylidenecaprolactam (24.7 %), butanol and dibutylacetal. The greater the proportion of caprolactam in the reaction, the greater the resulting butoxyethylidenecaprolactam and caprolactam hydrochloride content, and the less the butanol and dibutylacetol. The maximum butoxyethylidenecaprolactam yield (70%) is obtained at a 2 : 1 ratio of caprolactam to a-chloroether. Further increase in the caprolactam content of the reaction mixture leads to no further rise in yield, as it seriously complicates formation of the products and their liberation in pure form. The results obtained led us to the conclusion that the reaction between a-chloroethers and caprolactam proceeds in two stages. The first stage consists of the replacement of the excess caprolactam by the a-halide of halogenated ether (equation 1), and the second, of the combination of the liberated HCl with the initial caprolactam, which explains why twice as much of the latter is required.

$$CH_3-CHCl-OR + \underset{(CH_2)_5}{NH-CO} \rightarrow CH_3-\overset{OR}{\underset{(CH_2)_5}{CH-N-CO}} + HCl. \tag{1}$$
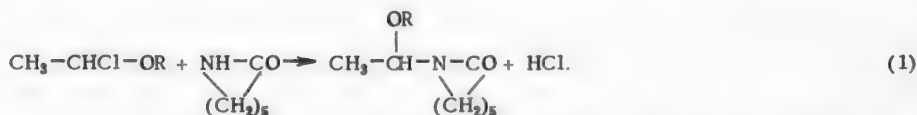
The high reactive capacity of the α-chloro ethers and their tendency to exchange the α-atom of chlorine for other atoms and groups is well known [1]. In the given instance this process is facilitated by the production of the crystalline hydrochloride, which is insoluble in the reaction mass. The presence of butanol and dibutylacetal in the reaction products may be explained by the partial decomposition of the α-chloro ether not reacted in equation (1). The possibility that a corresponding decomposition of the butoxyethylidenecaprolactam formed in the reaction may also take place must be considered as well. The following reaction mechanism is also possible in addition to that adduced above:

$$CH_3-CHCl-OR + \underset{(CH_2)_5}{NH-CO} \rightarrow CH_2=CH-OR + HCl \cdot \underset{(CH_2)_5}{NH-CO}. \tag{2}$$
$$\underset{(CH_2)_5}{NH-CO}$$
$$CH_3-CH(OR)\underset{(CH_2)_5}{N-CO}$$
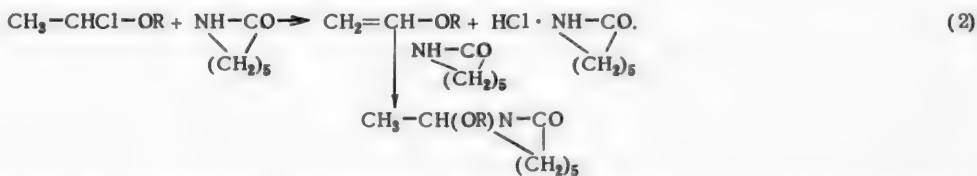
In the latter case the initial process is not exchange of the a-atom of chlorine, but splitting of the hydrogen halide. The second stage consists of addition of caprolactam to the vinyl butyl ether. The ability of a-halogenated ethers to split HX under the influence of organic bases has been described in various papers [1,2]. However, the first course seems the more probable to us, as: a) the alkalinity of caprolactam, as an amphoteric compound, cannot be high enough to cause the splitting off of hydrohalic acid; b) vinyl butyl ether was not liberated in a single experiment; and c), as will be seen below, the addition of caprolactam to vinyl butyl ether proceeds with difficulty and leads to a very negligible yield of alkoxyethylidenecaprolactam.

It is well known from the researches of our laboratory [3], that simple vinyl ethers of the $CH_2=CH-OR$ type readily combine with various substances containing a free hydrogen atom, if acid catalysts are present. This made it possible to postulate the successful combination of caprolactam with vinyl butyl ether. When they were heated in presence of minute quantities of hydrochloric acid we did obtain butyoxyethylidenecaprolactam, the yield, however, was exceedingly small (2.7 %). Butanol and dibutylacetal were obtained as by-products.

In an effort to extend the methods of synthesizing alkoxyethylidenecaprolactam, and to study the properties of the vinylcaprolactam previously obtained [4], we investigated the reaction caused when alcohols were added to the latter. Heating of vinylcaprolactam with methyl, ethyl and butyl alcohols in presence of an alkaline catalyst (KOH) failed to produce alkoxyethylidenecaprolactam. An approximately 8.5% yield of butoxyethylidenecaprolactam was produced when vinylcaprolactam was reacted with butanol in presence of hydrochloric acid under the conditions prescribed for the synthesis of dialkylacetal [5] (immediate mixture of the components).

$$CH_2=CH-\underset{\underset{(CH_2)_5}{\diagdown\diagup}}{N-CO} + C_4H_9OH \xrightarrow{H+} CH_3-\underset{\underset{(CH_2)_5}{\diagdown\diagup}}{\overset{\overset{OC_4H_9}{|}}{CH}-N-CO}. \tag{3}$$

There was no appreciable increase in yield when more severe conditions were applied (elevation of temperature and increased duration of the experiment): the reaction was accompanied by side-reactions (production of resins and disproportionation. However, these experiments demonstrated that the combination of alcohols strated with vinylcaprolactam proceeds in accordance with Markovnikov's law, as does their combination with vinyl alkyl ethers [4].

The ethoxy- and butoxyethylidenecaprolactam synthesized in this research are colorless viscous liquids which decompose upon distillation at atmospheric pressure. They hydrolyze into a dilute acid with the formation of acetaldehyde, caprolactam and the corresponding alcohol, as is confirmed by their structure.

$$CH_3-\underset{\underset{(CH_2)_5}{\diagdown\diagup}}{\overset{\overset{OR}{|}}{CH}-N-CO} + H_2O \xrightarrow{H+} CH_3CHO + ROH + \underset{\underset{(CH_2)_5}{\diagdown\diagup}}{NH-CO}. \tag{4}$$

Decomposition under heat, carried out with butoxyethylidenecaprolactam, was of considerable interest. Heating of this compund to 170 to 200° gave butanol and vinylcaprolactam (partially as monomer, partially as polymer):

$$CH_3-\underset{\underset{(CH_2)_5}{\diagdown\diagup}}{\overset{\overset{OC_4H_9}{|}}{CH}-N-CO}$$
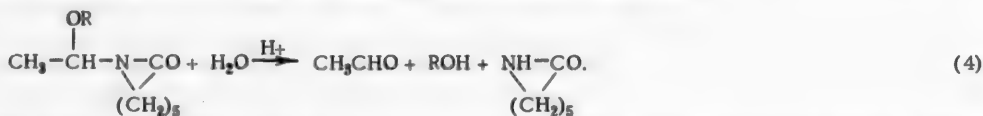
$$\xrightarrow{170-200°} CH_2=CH-\underset{\underset{(CH_2)_5}{\diagdown\diagup}}{N-CO} + C_4H_9OH \tag{5}$$

$$\xrightarrow{170-200°} CH_2=CH-OC_4H_9 + \underset{\underset{(CH_2)_5}{\diagdown\diagup}}{NH-CO} \tag{6}$$

Simultaneously with this main direction of reaction, decomposition also proceeds to a very limited degree in another manner, i.e., by the splitting of caplolactam and the liberation of inyl butyl ether (equation 6). Reactions 5 and 6 are further examples of indirect vinylation, as worked out by Shostakovsky and his associates [6].

EXPERIMENTAL

1. Reaction of a-chloroethyl butyl ether with caprolactam in 1 : 2 mole ratio. The a-chloroethyl butyl ether was produced from vinyl butyl ether and HCl [1] and possessed the following constants: b.p. 41-42°, 17 mm, n_D^{21} 1.4172. The caprolactam was purified by recrystallization from the ether and had a m.p. 67-68°.

The reaction was conducted in a flask with a stirrer, a thermometer and a reflux condenser, provided with a calcium chloride tube. A mixture of 32.6 g a-chloroether and 55.5 g benzene was added in the course of 2.5 hours to a solution of 70 g caprolactam in 140 ml anhydrous benzene, heated to 50°. The formation of small white crystals was noted within 20 to 30 minutes. When all the a-chloroether had been added the reaction mass was heated at 50° for another three hours and allowed to stand over night. The precipitated crystals of caprolactam hydrochloride were filtered out, washed in anhydrous ether and dried in a vacuum dessicator. The weight of the crystals was 33 g (91.4 %), m.p. 142-143° (from dichloroethane). The hygroscopicity of the crystals made it impossible to obtain a m.p. in a small interval.

Found %: HCl 23.85, 25.14. $C_6H_{12}ONCl$. Calculated %: HCl 24.37.

Neutralization of the hydrochloric caprolactam by a solution of caustic potash produced caprolactam, m.p. 67-68°; a sample mixed with caprolactam of known purity had m.p. 67°.

The benzene and ether filtrates obtained after the caprolactam hydrochloride was separated out, were neutralized with ammonia, the ammonium chloride was filtered out, and the solution washed five times in water, dried with potash and vacuum distilled. This gave 1.1 g dibutylacetal (b.p. 180-185°, n_D^{20} 1.4090), 36.6 g (71.9%) butoxyethylidenecaprola ctam (b.p. 116-117°, 2.8 mm), and 1.2 g resin. Salting out and distillation produced 19 g of the initial caprolactam from the washings. The botoxyethylidencaprolactam constants were:

n_D^{20} 1.4645, d_4^{20} 0.9774, MR_D 60.27; calculated 61.01.

Found %: N 6.77, 6.58; C 67.28, 67.54; H 11.04, 10.80, M 200.6, 199. $C_{12}H_{23}O_2N$. Calculated %: N 6.56; C 67.56; H 10.86. M 213.3.

2. Reaction of a-chloro ethyl butyl ether with caprolactam at 1:1 mole ratio. The reaction was produced by the method indicated in Experiment 1. 29.3 g of a -chloroether in 30 ml benzene was added to a solution of 25 g caprolactam in 50 ml benzene. The hydrochloric caprolactam was filtered out, and the filtrate put through the appropriate processes. This gave 2 g butanol (b.p. 115-117°, n_D^{20} 1.3999), 7.3 g dibutylacetal, 10.3 g (24.79%) butoxyethylidenecaprolactam and 7 g resin.

3. Reaction of a -chlorodiethyl ether with caprolactam. 20 g chlorodiethyl ether in 20 ml anhydrous benzene was added to 52 g caprolactam in 110 ml benzene under the conditions of Experiment 1. Crystals of hydrochloric caprolactam, b.p. 142-148°, were precipitated. Proces ing of the benzene filtrate, as in Experiment 1, gave 15 g (44%) ethoxyethylidenecaprolactam (b.p. 100-101°, 2.6 mm), 13.5 unreacted caprolactam and 1.5 g resin. The constants of the ethoxyethylidenecaprolactam were:

n_D^{20} 1.4806, d_4^{20} 1.0112, MR_D 52.13; calculated 51.77.

Found %: N 7.26, 7.35. $C_{10}H_{19}O_2N$. Calculated %: N 7.56.

4. Addition of caprolactam to vinyl butyl ether. 3 drops (0.05 g) concentrated HCl was added to a mixture of 33 g caprolactam, 29 g vinyl butyl ether and 40 ml dry acetone, heated to 53°; the mixture was boiled for ten minutes and allowed to stand overnight. When the solvent was driven off at 150 mm the following remained: a substance with a b.p. of 20-50° 50 mm and a viscous residue which crystallized rapidly. Distillation of the fraction of b.p. 20-50°, 50 mm, gave 17 g unreacted vinyl butyl ether: the undissolved portion consisted of 21.6 caprolactam, while dis tillation of the ether solution gave 1.5 g butanol, 1.5 g dibutylacetal and 1.7 g butoxyethylidene aprolactam (2.7%).

5. Addition of butanol to vinylcaprolactam. 2 drops concentrated HCl were added to a mixture of 21.3 g vinylcaprolactam and 17 g butanol, heated to 43 °; the temperature rose rapidly to 105°. This temperature was retained for five minutes, at which point heating was stopped and the reaction mass left over night. Neutralization with potash, and di stillation gave the following fractions: 1st, 35-95°, 4mm, 8 g; 2nd, 8 g 97-104°, 4 mm; 3rd, 18.2 g, 104-114° 4 mm; 2 g resinous residue; 1 g of product having n_D^{18} 1.4010, in the trap, cooled to −40°. The contents of the trap wer e merged with the 1st fraction and redistilled; 5.9 g butanol resulted. 13.6 g unreacted vinylcaprolactam, 1.8 g resin and 7.1 impure butoxyethylidenecaprolactam, from which 2.8 g (8.5%) of the pure product was obtained, were recovered from the 2nd and 3rd fractions. 0.5 g of a crystalline substance whose structure was not determined was formed in the resinous residue when permitted to stand.

6. Thermal decomposition of butoxyethylidenecaprolactam. 11.2 g butoxyethylidenecaprolactam was heated for two hours at 170-200° in a Favorsky retort, connected in series with a Liebig condenser, a receiver and a coil trap cooled to −40°. Distillation of the reaction mass in vacuum gave the following fractions: 1st, 36-92° 3.2 mm, 2 g; 2nd, 92-98° 3.2 mm, 2.8 g; 3rd, 98-108°, 3.2 mm, 6.2 g; n_D^{26} 1.4820. Trap contents − 1.5 g; resin 1.9 g.

Redisti llation and appropriate cleansing of the separate fractions (washing with water, drying with potash) gave 2g butanol, 1.3 g vinylcaprolactam (b.p. 93-97° 3.5 mm, n_D^{20} 1.5075). Bisulfite titration [7] established the vinylcaprolactam content − 97.8 (100.9%); 0.2 g caprolactam (m.p. 67-68°); approximately 0.2 g of a fraction with 50-95° b. p. with odor of vinyl butyl ether and demonstrating positive qualitative reactions for vinyl ethers; 0.7 g of a slightly tinted powder, having the characteristic qualities [4] of polyvinylcaprolactam, was recovered from the resi nous residue upon processing with ethyl ether.

3.803 mg substance: 14.1 ml 0.02 N KH(IO₃)₂. Found %: N 10.34. $(C_8H_{13}ON)_n$. Calculated %: N 10.07.

7. Hydrolysis of butoxyethylidenecaprolactam. 10 g butoxyethylidenecaprolactam and 100 ml 2% H_2SO_4 were heated for 3 hours at 80° in a retort with reflux condenser under constant stirring and ventilation with a nitrogen stream. The reflux condenser was connected with three ice-cooled Tishchenko flasks, each containing 40 ml water. Wit hin 30 minutes the reaction mass became homogenous. When heating was concluded, the reaction product was neutralized with barium carbonate, the $BaSO_4$ was filtered out, and the filtrate distilled. This gave a fraction with

b.p. 92-98°, from which 3.1 g butanol and a resinous residue were obtained. Boiling ether extraction of the resin gave 3.3 g caprolactam with m.p. 67°.

The contents of the Tishchenko flasks gave a residue of 2,4-dinitrophenylhydrazone acetaldehyde (m.p. 159°, from alcohol). Bisulfite titration of an aliquot portion gave 0.9599 g acetaldehyde.

8. Hydrolysis of ethoxyethylidenecaprolactam. 9.8 g ethoxyethylidenecaprolactam was hydrolyzed in presence of sulfuric acid. The reaction procedure and separation of the products followed that in Experiment 7, 2.5 g caprolactam with m.p. 67-68° was recovered. An acetaldehyde derivative, m.p. 157° (from alcohol) was produced by reacting the solutions collected from the Tishchenko absorption flasks with 2,4-dinitrophenylhydrzzine. On bisulfite titration 1.533 g acetaldehyde was found.

SUMMARY

1. Reaction of caprolactam with a-chloroethyl butyl and a-chlorodiethyl ether produced butoxy- and ethoxyethylidenecaprolactams with a yield of up to 70% of the theoretical .

2. It was shown that addition of caprolactam to vinyl butyl ether, and also addition of butanol to vinylcaprolactam with the purpose of synthesizing butoxyethylidenecaprolactam proceeded very slowly and did not result in a satisfactory yield of the product sought.

3. Synthesized alkoxyethylidenecaprolactams hydrolyze in presence of sulfuric acid with the production of alcohol, caprolactam and acetaldehyde.

4. It was shown that vinylcaprolactam and butanol are the major thermal decomposition products of butoxyethylidenecaprolactam.

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REACTION OF SODIUM SALTS OF CARBOXYLIC ACIDS IN MELTS

N. M. Sokolov

Various methods of physical chemical analysis have been applied to the study of a number of double and more complex salt systems in melts. These studies have permitted our native scientists to deduce certain laws of the direction of processes in salt melts. All these researches have been performed with systems consisting of inorganic acid salts. Study of carboxylic acid salts has been completely inadequate in this regard. Only two systems have been described in the literature. Baskov described the potassium acetate – sodium acetate system in 1915 [1], and a description of a second system, sodium acetate – zinc acetate, appeared rather recently [2].

The purpose of the present work was to employ the visual-polythermic method in studying double systems consisting of the sodium salts of carboxylic acids.

In studies of this type, the reaction of the salt to heating is of decisive importance. Only systems whose components do not decompose upon heating may be studied. Among carboxylic acid sodium salts, only sodium acetate and formate have been thoroughly studied in this regard. According to the literature [3], sodium formate does not decompose after heating to 310° for five hours, and decomposes very slowly at 400°. The addition of caustic alkali greatly accelerates decomposition of the formate [4]. Anhydous sodium acetate, which melts at 331°, may be heated to 390° [5], but at higher temperatures it decomposes into soda and acetone [6]. The addition of an alkaline caustic also facilitates decomposition of this acetate. In general, a mixture of carboxylic acid sodium salt and an alkaline caustic produces a hydrocarbon and soda upon calcination [7]. Sodium formate, acetate and propionate melt and solidify upon cooling as do inorganic acid salts, i.e., heating causes them to change directly from the solid crystalline to the amorphous liquid state, while cooling from the melt results in solid crystals. However, according to the findings of certain writers, the melting and solidification of carboxylic acid salts containing three or more carbon atoms in the radical proceeds differently. Upon fusing sodium stearate, Adami and Aschoff [9] observed a liquid crystalline phase intermediate between the solid crystalline and the liquid amorphous. Vorländer [8] found a liquid crystalline phase in the majority of organic acid salts having three or more carbon atoms in the radical. These salts have, as it were, two melting points: one representing the transition from the solid crystalline to the liquid crystalline phase, and the second, from the liquid crystalline to the liquid amorphous. They found the following approximate melting points for salts that are components of the systems we studied: 250° and 320° for sodium isobutyrate, 210 and 310° for sodium butyrate, 168 and 260° for sodium isovalerate, 225 and 350 for sodium caproate, 220 and 305° for sodium stearate, and 410 and 430 for sodium benzoate. Vorländer obtained his salts by mixing equivalent quantities either of base and acid (in the presence of a trace of phenolphthalein), or of alcoholate and acid. Acid, base and alcoholate were all used in alcoholic solutions. Neutralization of the base by the acid caused concentration of the salt solution, and when the alcoholate was used the salt was displaced from the alcohol by ether. In our opinion, the difficulty of determining the equivalent point under these conditions, and also the use of equivalent quantities of substances to obtain the salts, create the possibility that salt obtained in this way may be contaminated by alkali or acid. Therefore we obtained our salts by reacting an excess – always – of acid with an aqueous soda solution; the aqueous salt solution was concentrated, and the salt was then dried to complete elimination of excess acid.

Slow cooling of transparent melts of these salts in test tubes accompanied by constant stirring with a fine glass stirrer resulted first in clouding, and then in the formation of a pasty mass which solidified during a specific temperature interval. Sodium formate, acetate and isobutyrate separated out as crystals upon cooling from melts, as do inorganic acid salts. We took as the melting point (the point at which the first crystals appeared) for both pure salt and salt mixtures the temperature at which the homogeneity of the melt disappeared. In some cases this corresponded to the appearance of clouding, and in others to the appearance of crystals.

EXPERIMENTAL

For optimum uniformity of heating, the test tube containing the salts was placed in a larger test tube. A glass filament (mixer) was placed in the test tube containing the salts, and the hot point of a nichrome-constantan thermo-

couple was placed in the glass jacket; the other point was placed in a Dewar flask at a specific temperature. The thermocouple was connected to a mirror-scale galvanometer at 17 millivolts.

To translate the millivoltmeter scale information into degrees of temperature, a datum point curve was plotted on the basis of the following melting points: benzoic acid 122.5°, mannitol 166°, tin 232°, cadmium 321°, potassium nitrate 337°, potassium bichromate 397.5°, zinc 419.5°, lead chloride 498°, and the boiling point of sulfur, 444.6°. Based on this datum point curve the melting points (the temperature of onset of crystallization) of the components were: sodium formate 258°, sodium acetate 331°, sodium butytate 330°, sodium isobutyrate 260°, sodium isovalerate 262°, sodium caproate 365°, sodium stearate 308°, and sodium benzoate 463°.

Commercial sodium acetate, sodium stearate and sodium benzoate were used. The remaining salts were synthesized by us, starting with sodium carbonate solution and the particular acid. The sodium carbonate and acid were first purified by distillation. To produce the salt, the acid was added, bit by bit, with constant stirring, to the aqueous sodium carbonate solution (cold when the formate was desired, and hot for synthesis of the remaining salts) first until a neutral reaction was obtained; a one or two ml excess of acid was then added, until litmus paper gave a clearly acid reaction. The salt solution was evaporated to dryness in a porcelain cup over a water bath. The dry residue was carefully pulverized and dried in a desiccator at 160° until the acid odor disappeared completely. When acid (acid salt) admixture was missing, the salt solution showed a clearly basic reaction on litmus paper, and, in the second place, the same sample of salt showed no change in melting point upon several consecutive melts. A salt with acid impurity, or acid salt showed an increased melting point at each new melt, and drops of water would appear on the sides of the test tube as a result of liberation of acid or decomposition of the acid salt. When salt is obtained in this manner it is absolutely essential to use excess acid. If a salt solution obtained by mixing equivalent portions of soda and acid be evaporated, the dry residue will darken when heated in a desiccator, and when subjected to melting will decompose before reaching the melting point. When this occurs the decomposition of the salt is most probably due to an admixture of alkali. Evaporation results in partial hydrolysis of the salt, and the acid formed is volatilized with the water vapor, while the alkali remains to contaminate the salt. Removal of the excess acid during synthesis of sodium formate, isobutyrate, butyrate and caproate presented no difficulty. Elimination of the excess acid proved more difficult during isovalerate synthesis due to the tendency of this compound to produce stable acid salts. In this instance the residue after drying was carefully melted, without overheating, poured over a hot plate in a thin layer, and pulverized while hot.

Desiring to trace the effect of the salt hydrocarbon radical upon the processes of fusion, we divided the systems investigated into seven groups. In each of these groups, one component was identical for all systems.

The systems containing sodium benzoate were not studied fully, but only to a given sodium benzoate content, as further addition of this compound led to a rise in the temperature of fusion of the mixture, and to its decomposition. It was not possible to add other salts to the benzoate because of its high melting point (463°), at which other salts decompose.

All compositions are given in molecular percentages.

1. Systems with sodium formate.

The fusibility curve of the sodium formate-sodium acetate system (Fig. 1), Table   consisted of two branches, intersecting at a eutectic point reached at 242° and 10.5% acetate.
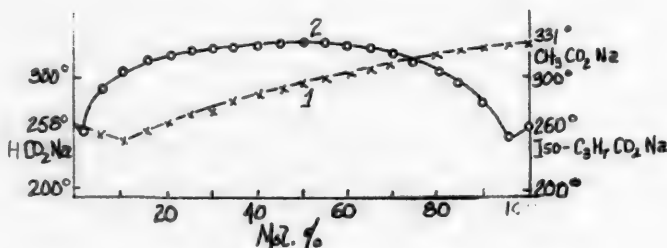

Fig. 1. Fusibility curves of systems:

1) Sodium formate — sodium acetate; 2) sodium formate — sodium isobutyrate.

Three branches of the crystallization curve in the sodium formate-sodium butyrate system (Fig. 2, Table 1) intersect at two eutectic points: 252° and 2.5% butyrate, and 318° and 89% butyrate. A compound that fused without decomposition was formed: $HCOONa \cdot C_3H_7COONa$. The fusibility curve of the sodium formate—sodium isobutyrate system (Fig. 1, Table 1) consist of three segments intersecting at two eutectic points: 252° and 1.3% isobutyrate,

TABLE 1

Acetate (%)	Onset of crystall- ization	Butyrate (%)	Onset of crystall- ization	Isobutyrate (%)	Onset of crystall- ization	Isovalerate (%)	Onset of crystall- ization
0	258°	0	258°	0	258°	0	258°
5	252	2.5	252	1.3	252	0.75	252
10	244	5	287	5	290	5	287
10.5	242	10	301	10	305	10	300
15	252	15	312	15	314	15	308
20	260	20	318	20	319	20	311
25	267	25	324	25	321	25	314
30	270	30	327	30	324	30	316
35	278	35	333	35	326	35	318
40	284	40	337	40	327	40	320
45	291	45	339	45	329	45	319
50	296	50	341	50	330	50	317
55	300	55	340	55	329	55	315
60	303	60	340	60	327	60	312
65	308	65	339	65	325	65	309
70	313	70	338	70	320	70	306
75	316	75	336	75	314	75	301
80	320	80	331	80	306	80	297
85	323	85	324	85	296	85	284
90	326	89	308	90	282	90	265
95	330	90	311	95	258	94.5	245
100	331	95	322	96.5	250	100	262
		100	330	100	260		

and 250° and 96.5% isobutyrate. A compound was formed that fused without decomposition: $HCOONa \cdot iso\text{-}C_3H_7COONa$. The sodium formate — sodium isovalerate system has three curves of crystallization, intersecting at two eutectic points: at 252° and 0.75% isovalerate, and at 245° and 94.5% isovalerate. The following compounds, which fuse without decomposition, were formed $3HCOONa \cdot 2\ iso\text{-}C_4H_9COONa$ (Fig. 2, Table 1).

Sodium caproate proved to be negligibly soluble in the fused formate in a sodium formate-sodium caproate system. Sodium formate decomposed upon being added to fused sodium caproate.

In the sodium formate-sodium stearate system, the components would not mix when fused.

In the sodium formate-sodium benzoate system, the latter was not soluble in the former when fused. Upon heating to the melting point of the benzoate, the formate decomposed.
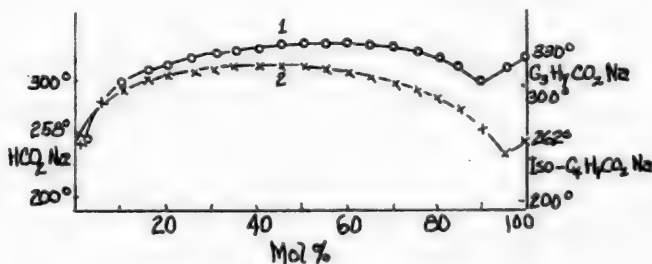
Fig. 2. Fusibility curves of systems:
1) Sodium formate—sodium n-butyrate; 2) sodium formate—sodium isovalerate.

The data obtained by study of the systems comprising sodium formate (Table 1) show that: 1) sodium acetate, butyrate, isobutyrate and isovalerate, when fused, were miscible with sodium formate; the caproate and stearate were not miscible. It is possible that other fatty acid salts containing more than five carbon atoms in the radical may not be miscible in melts with formate. Neither did sodium benzoate mix with the formate in a melt. 2) An increase in the number of carbon atoms in the radical of a fatty acid salt facilitates complex formation. Sodium acetate and butyrate, having very similar melting points (331 and 300°) reacted differently with the formate. Complex formation did not occur in the sodium formate-sodium acetate system, but it did with the others. 3) Branching of the carbon chain without variation in the number of carbon atoms in the radical does not affect the nature of the reaction between salts and sodium formate; complex formation was noted in systems embracing the butyrate and the isobutyrate. 4) A rise in the number of carbon atoms in the radical of the second component in these systems brings a reduction in the primary crystallization of the formate side. Thus, in the system formed with the acetate, the share of the formate was 10.5%, with butyrate it was 2.5%, and with isovalerate it was only 0.75%.

2. Sodium acetate systems.

The three curves of crystallization (Fig. 3, Table 2) in the sodium acetate-sodium butyrate system are intersected at two eutectic points, 266° and 33.5% butyrate, and 250° and 69% sodium butyrate. The compound formed was $3CH_3COONa \cdot 2C_3H_7COONa$.
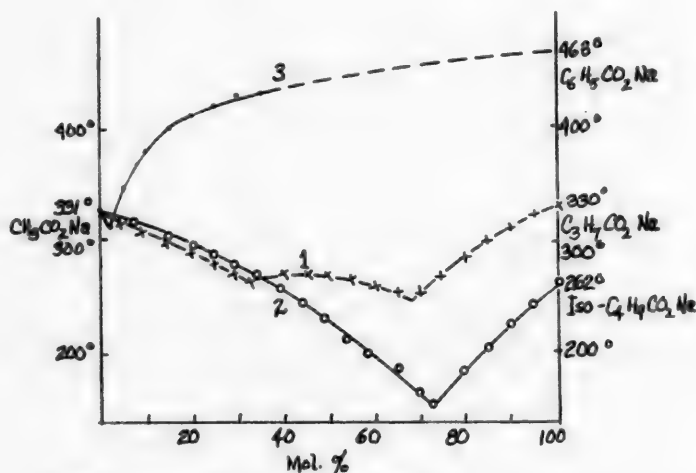

Fig. 3. Fusibility curve of the system.
1) Sodium acetate and sodium butyrate; 2) sodium acetate and sodium isovalerate; 3) sodium acetate and sodium benzoate.
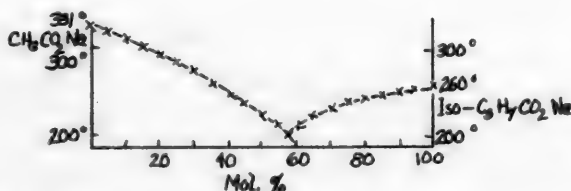

Fig. 4. Fusibility curve of sodium acetate—sodium isobutyrate.

TABLE 2

Butyrate (%)	Onset of crystallization	Isobutyrate (%)	Onset of crystallization	Isovalerate (%)	Onset of crystallization	Caproate (%)	Onset of crystallization	Benzoate (%)	Onset of crystallization
0	331°	0	331°	0	331°	0	331°	0	331°
5	319	5	323	5	320	5	321	2.6	315
10	309	10	314	10	311	10	312	5	350
15	299	15	305	15	304	15	304	10	380
20	290	20	297	20	295	20	296	15	400
25	282	25	288	25	287	25	288	20	411
30	274	30	277	30	280	30	279	25	421
33.5	266	35	265	35	269	34.5	268	30	428
35	268	40	254	40	260	35	269	33	431
40	273	45	242	45	248	40	269	100	465
45	270	50	230	50	232	45	265		
50	268	55	218	55	215	49.5	260		
55	265	58	208	60	199	50	265		
60	260	60	215	65	184	55	300		
65	254	65	226	70	166	60	321		
69	250	70	236	73	156	65	332		
70	253	75	242	75	163	70	342		
75	266	80	246	80	185	75	349		
80	281	85	250	85	207	80	353		
90	312	90	254	90	228	90	360		
95	324	95	257	95	247	95	363		
100	330	100	260	100	262	100	365		

The sodium acetate-sodium isobutyrate system fusibility curve shows two branches (Fig. 4, Table 2) intersected at a eutectic point, 208° and 58% sodium isobutyrate.

The two branches of the fusibility curve of the sodium acetate-sodium isovalerate system are intersected at a eutectic point at 156° and 73% sodium isovalerate.

The three branches of the fusibility curve of the sodium acetate-sodium caproate system (Fig. 5, Table 2) are intersected at two eutectic points at 268° and 34.5% sodium caproate, and 260° and 49.5% sodium caproate. The compound formed was $5CH_3COONa \cdot 3C_5H_{11}COONa$.

The sodium acetate-sodium benzoate system, studied only up to 33% benzoate content, shows two branches of crystallization (Fig. 3, Table 2), intersecting at a eutectic point at 315° and 2.6% sodium benzoate.
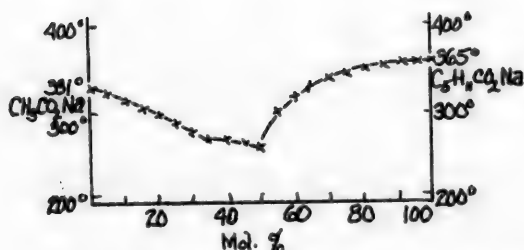

Fig. 5. Fusibility curve of sodium acetate—sodium caproate system.
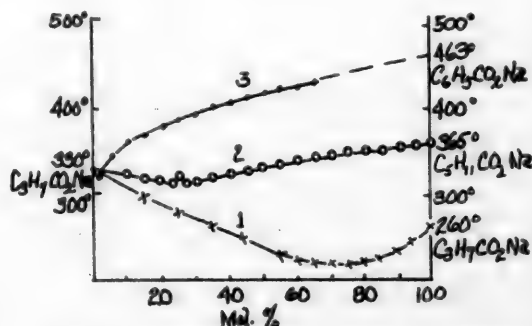

Fig. 6. Fusibility curves of systems: 1) Sodium butyrate—sodium isobutyrate; 2) sodium n-butyrate—sodium caproate; 3) sodium n-butyrate—sodium benzoate.

In a sodium acetate-sodium stearate system, these compounds failed to mix in the fused state.

The research data for systems formed with sodium acetate show that: (1) sodium formate, butyrate, isobutyrate, isovalerate, caproate and benzoate are miscible with sodium acetate in melts. Sodium stearate is not miscible. (2) Complex formation is observed in systems whose second component is the salt of a fatty acid with unbranched carbon atom chain in the radical. Thus, sodium butyrate and caproate combine with sodium acetate to produce: $3CH_3COONa \cdot 2C_3H_7COONa$ and $5CH_3COONa \cdot 3C_5H_{11}COONa$. (3) Complex formation does not take place in the systems whose second component is the salt of a fatty acid with a branched carbon atom chain in the radical; sodium isobutyrate and isovalerate do not form compounds with sodium acetate. Sodium acetate decomposed spontaneously when heated above 390°, while in a system with the benzoate it resisted decomposition up to 430°.

3. Systems with sodium butyrate.

The sodium butyrate-sodium isobutyrate system formed an uninterrupted series of solid solutions from a minimum at 221° and 72.5% sodium isobutyrate (Fig. 6, Table 3).

The two branches of the fusibility curve in the sodium butyrate-sodium isovalerate system (Fig. 7, Table 3) intersected at a eutectic point at 257° and 90.5% sodium isovalerate.

TABLE 3

Isobutyrate, (%)	Onset of crystallization	Isovalerate,(%)	Onset of crystallization	Caproate, (%)	Onset of crystallization	Stearate, (%)	Onset of crystallization	Benzoate, (%)	Onset of crystallization
0	330°	0	330°	0	330°	0	330°	0	330°
5	317	5	326	5	328	5	289	0.13	330
10	306	10	323	10	324	10	261	5	349
15	297	15	320	15	320	15	248	10	361
20	287	20	316	20	318	20	277	15	370
25	279	25	312	22.5	317	25	317	20	378
30	270	30	308	25	321	30	351	25	386
35	264	35	305	27.5	317	35	379	30	394
40	257	40	300	30	319	40	390	35	401
45	250	45	295	35	323	45	389	40	408
50	242	50	292	40	326	50	386	45	415
55	235	55	287	45	331	55	380	50	421
60	229	60	284	50	334	60	376	55	427
65	224	65	281	55	340	65	370	60	434
70	222	70	277	60	343	70	364	100	463
72.5	221	75	273	65	344	75	358		
75	222	80	269	70	349	80	350		
80	225	85	263	75	353	85	340		
85	228	90	258	80	356	90	330		
90	235	90.5	257	85	359	95	314		
95	248	95	263	90	360	96.5	309		
100	260	100	262	95	363	98.5	312		
				100	365	100	308		

The fusibility curve of the sodium butyrate-sodium caproate system has three branches, intersecting at two eutectic points: at 317° and 22.5% sodium caproate and at 317° and 27.5% sodium caproate (Fig. 6, Table 3). The following compound was formed: $4C_3H_7COONa \cdot C_5H_{11}COONa$.

The three branches of crystallization of the sodium butyrate-sodium stearate system (Fig. 7, Table 3) intersect at a eutectic point at 248° and 15% sodium stearate, and at a transition point, 309° and 96.5% sodium stearate. The compound formed was $3C_3H_7COONa \cdot 2C_{17}H_{35}COONa$.

The sodium butyrate-sodium benzoate system, studied only to 60% benzoate content, shows two branches in its fusibility curve, intersected at 330° and 0.13% sodium benzoate.

The results of the studies of systems with sodium butyrate show that: (1) all the fatty acid salts we studied, and sodium benzoate, were miscible with sodium butyrate; (2) complex formation occurred in systems where the second component was a fatty acid salt whose radical contained a straight carbon chain; (3) complex formation did not occur in systems whose second component was a fatty acid salt whose radical contained a side chain.

In the sodium isobutyrate-sodium benzoate system, studied only to 80% sodium benzoate content, the fusibility curve (Fig. 9, Table 4) has two branches, which intersect at a eutectic point at 228° and 3.5% sodium benzoate.

Comparison of the data of systems containing sodium isobutyrate shows that: (1) all the salts studied were miscible in melts with sodium isobutyrate; (2) sodium isobutyrate, whose radical contains a branched carbon atom chain, formed complexes with the formate and the stearate; (3) an uninterrupted series of solid solutions was formed between sodium isobutyrate and sodium butyrate, from whih it differs in melting point and structure of radical, but with which it is identical in the number of carbon atoms in the radical; (4) the isobutyrate also formed an uninterrupted series of solid solutions with sodium isovalerate. These two salts have similar melting points and radicals of analogous structure.

5. Systems with sodium isovalerate.

The sodium isovalerate-sodium caproate system formed an uninterrupted series of solid solutions with a minimum at 239° and 20% sodium caproate (Fig. 10, Table 5).

The three branches of primary cyrstallization in the sodium isovalerate-sodium stearate system are intersected at two points: the eutectic at 140° and 17.3% sodium stearate, and the transitional, at 309° and 92% sodium stearate. The compound formed was iso-C_4H_9COONa · $2C_{17}H_{35}$COONa.
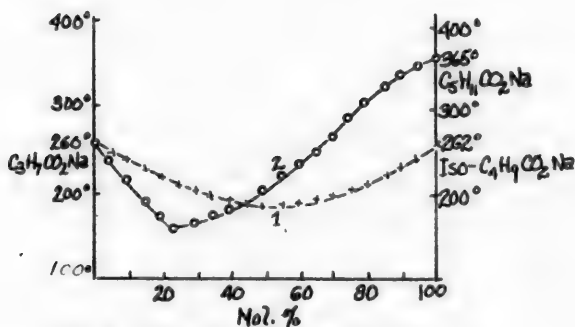
Fig. 8. Fusibility curve of the system:
1) Sodium isobutyrate−sodium isovalerate.
2) sodium isobutyrate−sodium caproate.
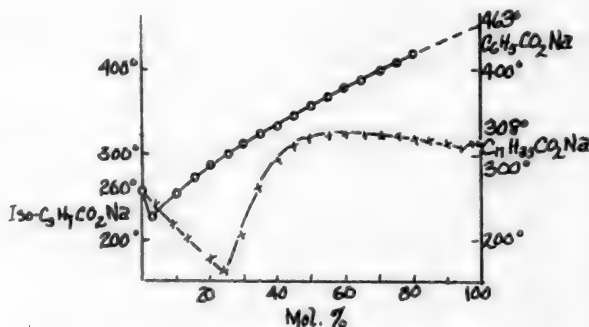
Fig. 9. Fusibility curve of the system:
1) Sodium isobutyrate−sodium stearate.
2) sodium isobutyrate−sodium benzoate.

The sodium isovalerate-sodium benzoate system was studied up to 70% sodium benzoate content. The fusibility curve has two branches, intersecting at 261° and 3% sodium benzoate (Fig. 10, Table 5).
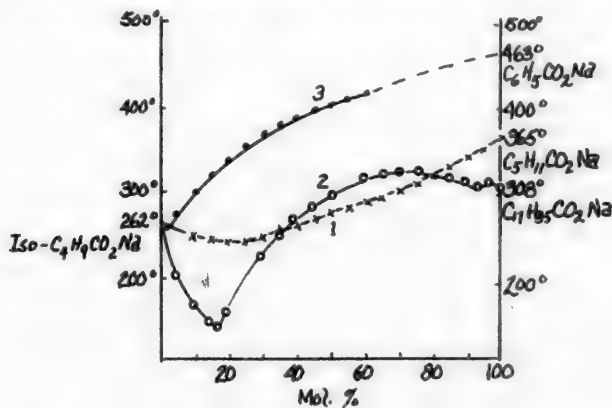
Fig. 10. Fusibility curves of systems:
1) Sodium isovalerate−sodium caproate; 2) sodium isovalerate−
−sodium stearate; 3) sodium isovalerate−sodium benzoate.
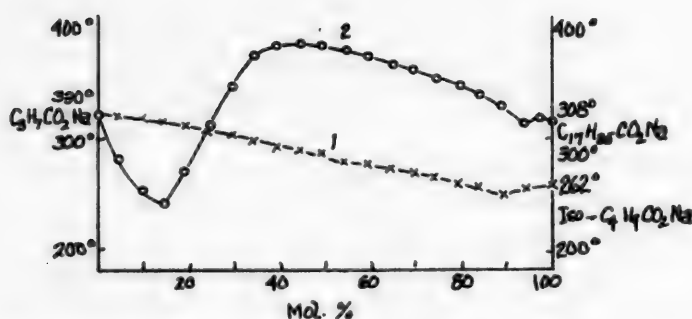
Fig . 7. Fusibility curves of systems;
1) Sodium butyrate—sodium isovalerate;
2) Sodium butyrate, sodium stearate.

4 . Systems with sodium isobutyrate

The sodium isobutyrate-sodium isovalerate system formed an uninterrupted series of solid solutions, starting at 189° and 50% sodium isovalerate (Fig. 8, Table 4).

T A B L E 4

Isoval-erate,(%)	Onset of crystall-ization	Caproate, (%)	Onset of crystall-ization	Stearate, (%)	Onset of crystall-ization	Benzoate, (%)	Onset of crystall-ization
0	260°	0	260°	0	260°	0	260°
5	248	5	237	5	240	3.5	228
10	238	10	218	10	215	5	235
15	229	15	195	15	196	10	256
20	220	20	175	20	177	15	272
25	213	23.5	160	25	163	20	288
30	207	25	161	25.5	162	25	301
35	201	30	168	30	217	30	312
40	197	35	175	35	260	35	322
45	193	40	182	40	291	40	335
50	188	45	191	45	309	45	344
55	189	50	205	50	319	50	355
60	191	55	220	55	321	55	367
65	194	60	235	60	323	60	379
70	199	65	252	65	322	65	389
75	207	70	270	70	321	70	399
80	215	75	290	75	320	75	408
85	225	85	329	85	317	100	463
90	237	90	345	90	314		
95	248	95	356	94.5	311		
100	262	100	365	97.5	312		
				100	308		

The two branches of primary crystallization in the sodium isobutyrate-sodium caproate system (Fig. 8, Table 4) are intersected at 160°. and 23.5% by sodium caproate.

The three branches of crystallization in the sodium isobutyrate-sodium stearate system (Fig. 9, Table 4) are intersected at a eutectic point at 162° and 25.5% sodium stearate, and at a transition point at 312° and 97.5% sodium stearate. The compound formed was 2-iso-C_3H_7COONa · 3$C_{17}H_{35}$COONa.

Fig. 11. Fusibility curves of systems:
1 - sodium caproate—sodium stearate;
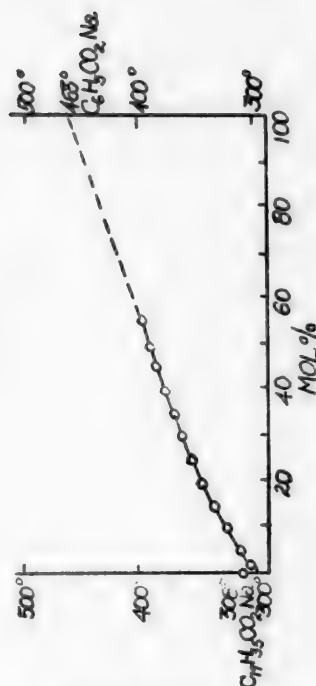2 - sodium caproate—sodium benzoate.

Fig. 12. Fusibility curve of sodium stearate—sodium benzoate system.

TABLE 5

Caproate %	Onset of crystalliza-tion	Stear-ate %	Onset of crystalliza-tion	Benzoate %	Onset of crystalliza-tion
0	262°	0	262°	0	262°
5	255	5	201	3	261
10	247	10	167	5	275
15	243	15	147	10	298
20	239	17.3	140	15	317
25	242	20	162	20	337
30	248	30	225	25	349
35	256	35	247	30	365
40	263	40	266	35	379
45	271	45	282	40	389
50	277	50	295	45	396
55	283	55	305	50	401
60	291	60	315	55	407
65	296	65	322	60	415
70	304	70	323	65	421
75	313	75	321	70	426
80	322	85	318	100	463
85	331	90	314		
90	341	93.5	309		
95	354	95	312		
100	365	100	308		

The results of studies of systems with sodium isovalerate show that: (1) all the salts we studied were miscible with sodium isovalerate in melts; (2) sodium isovalerate, whose radical has a split chain, reacted to form compounds with sodium formate and sodium stearate, but did not combine with the remaining salts.

6. Systems with sodium caproate.

The three branches of primary crystallization of the sodium caproate—sodium stearate system (Fig. 11, Table 6) are intersected at two points: the eutectic at 239° and 17.5% sodium stearate, and the transitional at 314° and 94.5% sodium stearate. The compound formed was:

$$2C_5H_{11}COONa \cdot 3C_{17}H_{35}COONa$$
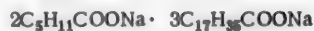
The sodium caproate—sodium benzoate system, studied to 40% sodium benzoate content, has two branches in its fusibility curve, intersected at a transition point of 371° and 13% sodium benzoate.

Comparison of the data for the systems with sodium caproate show that: (1) fused sodium caproate reacted with all the salts under study, except sodium formate; (2) complexes were formed in systems whose second component was a salt with a radical of normal structure; and (3) complexes were not formed in systems whose second component contained a radical with branched chain.

1575

TABLE 6

Stearate (%)	Onset of crystallization	Stearate, (%)	Onset of crystallization	Stearate, (%)	Onset of crystallization	Benzoate, (%)	Onset of crystallization
0	365°	35	293°	75	326°	0	365°
5	320	40	305	80	324	5	369
10	272	45	313	85	321	10	373
15	242	50	320	90	319	13	371
17.5	239	55	326	94.5	314	15	374
20	248	60	329	95	316	20	380
25	264	65	328	100	308	35	396
30	280	70	327			40	400
						100	463

7. System with sodium stearate

Sodium stearate-sodium benzoate system

Sodium benzoate, %	0	1.3	5	10	15	20	24
Onset of crystallization	308°	301	310	321	332	344	353
Sodium benzoate, %	30	35	40	45	50	55	100
Onset of crystallization	362°	369	376	384	390	396	463

The system was studied up to 55% sodium benzoate content. The two branches of the fusibility curve intersect at a eutectic point at 301° and 1.3% sodium benzoate (Fig. 12).

Examination of the results of studies of systems containing sodium stearate, we conclude that the large difference in radical size facilitates complex formation. Thus, the stearate combined with all the fatty acid salts with which it was miscible in melts. This conclusion is confirmed in systems with the formate, as there, too, complexes were formed where there were large differences in radical dimensions. When the difference between radical dimensions was large, the radical structure did not have an important effect upon the character of the reaction. Thus, the formate-butyrate, formate-isobutyrate formate-isovalerate systems resembled each other very closely. This was also true in the stearate systems, whose fusibility curves also show mutual similarity.

Complex formation does not take place, in all probability, in systems containing sodium benzoate.

SUMMARY

28 binary systems formed by carboxylic acid sodium salts were studied. Certain laws were established relative to the effect of the structure of the paraffin portion of carbon acid salt molecules upon processes occurring in salt melts.

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ISOMERIZATION OF METHYLCYCLOHEXANE OVER AN
ALUMINOSILICATE CATALYST

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The isomerization of methylcyclohexane has been studied by a number of researchers [1-3], who established that in the presence of aluminum chloride it undergoes isomerization with a narrowing of the ring in the cyclo-heptane derivatives, the yield at best being 6.3% [4]. Later, Zelinksy and Turova-Polyak [5], studying the isomerization of cyclohexane homologs, particularly methylcyclohexane, in the presence of aluminum chloride, concluded that this catalyst causes virtually no noticeable change in methylcyclohexane.

In view of the fact that the isomerization of naphthene hydrocarbons encountered in petroleum is closely related to the problem of changes in petroleum in nature, it appeared to be of interest to study the isomerization of methylcyclohexane over a natural aluminosilicate catalyst at a temperature not over 250°, particularly as certain researchers [6,7] see an analogy in the isomerization effect of aluminum chloride and of natural aluminosilicate catalysts.

As we have demonstrated [8], this is true of cyclohexane, which undergoes 37 to 40% isomerization to methyl-cyclopentane at 245-250° under the influence of activated gumbrin, confirming the findings of Nenitzescu and Cantu-niari [9], who obtained 22% methylcyclopentane by isomerizing cyclohexane over aluminum chloride. According to Zelinsky [10], cyclohexane undergoes 23.5-24% isomerization to methylcyclopentane in the presence of aluminum chloride.

The methylcyclohexane used in our studies possessed the following constants: b.p. 100.5° (756 mm), d_4^{20} 0.7685, n_D^{20} 1.4235 and contained 0.40% aromatic hydrocarbons (by the aniline method). Equal weights of methylcyclohexane and hydrochloric acid-activated gumbrin (a clay of the montmorillonite type) were placed in a 500 ml high-pressure autoclave and heated by an electric furnace to 245-250°. The duration of heating in various experiments was 50, 70, 90 and 110 hours. Maximum pressure during the experiments did not exceed 25 atm, and fell to zero after cooling of the autoclave. No gas formation was observed in any experiment. At the conclusion of the experiment the product had blended with the catalyst. The product bound by the catalyst was blown out with hot air, freed of water and combined with the general mass. Specific gravity and refractive index were determined after filtration and drying, in order to establish the depth of isomerization of methylcyclohexane (Table 1).

The isomerization products of the first three experiments were distilled in a 100-cm-high Vigreaux fractionating column, five fractions being obtained:) 1st, to 85°; 2nd, 85-90°; 3rd, 90-95°; 4th, 95-100°; 5th, 100-103°.

The first fractions of three experiments, boiling at 44 to 85°, were combined (5.8 g) and distilled in a column with an efficiency of 25 theoretical plates, at the following intervals:

Fraction No.	Boiling point	Weight of fraction (g)	n_D^{20}
1	36-44°	0.39	1.3560
2	44-58	0.06	1.3708
3	58-65	0.59	1.3790
4	65-70	0.92	1.3910
5	70-78	0.95	1.4060
6	78-82	0.48	1.4095
	Residue	1.31	-
	Losses	1.10	-

The fraction boiling at 36-44° corresponded to n-pentane (b.p. 36.8°, n_D^{20} 1.3577) according to its refractive index. The fraction ghat boiled off at 58-65° contained 3-methylpentane (b.p. 63.2°, n_D^{20} 1.3765). The 65-70° fraction corresponded, judging by its refractive index, to a mixture of n-hexane (b.p. 68.8°, n_D^{20} 1.3750) and methylcyclopen-tane (b.p. 71.9°, n_D^{20} 1.4099). The 70-78° fraction apparently consisted primarily of methylcyclopentane.

The second (85-90°) and third (90-95°) fractions of the catalyzate in the three experiments were combined (63.1 g) and distilled in the same column. Quadruple distillation resulted in the isolation of 24.5 g of a product that boiled

TABLE 1

Heating time (hours)	Methyl-cyclo-hexane charge (g)	Yield of prod-uct, %	Constants of the reaction products		Aromatic hydrocar-bons, %
			d_4^{20}	n_D^{20}	
50	120	90.83	0.7610	1.4199	0.70
70	120	90.19	0.7600	1.4186	1.11
90	120	89.60	0.7588	1.4180	—
110	120	91.40	0.7585	1.4185	0.78

between 90.1-90.5° and had the following constants: d_4^{20} 0.7466, n_D^{20} 1.4105. According to its constants this fraction lay between 1,3-dimethylcyclopentane (d_4^{20} 0.7456, n_D^{20} 1.4092) and trans-1,2-dimethylcyclopentane (d_4^{20} 0.7519, n_D^{20} 1.4117). The composition of this fraction was studied by the Raman spectrum method.

The spectrum of this fraction is given below, together with those of 1,3-dimethylcyclopentane and trans-1,2-dimethylcyclopentane (as given by Bazhulin [11].

Spectrum of 1,3-dimethylcyclopentane	Spectrum of 90.1-90.5° fraction	Spectrum of trans-1,2-dimethylcyclopentane
213(0), 272(0), 358(0), 373(3,w), 419(0), 426(3,w), 514(13), 549(3), 591(3,dl.) 726(0), 803(13,6), 828(28), 878(0), 950(3), 985(8), 1021(3,w), 1041(3,w), 1085(3), 1100(3), 1140(11), 1152(11), 1188(2,w), 1250(0), 1298(2,w), 1314(8), 1346(5,dl), 1457 (40,w), 2725(4), 2847(100,w),(2867), (220), 2905(101), 1925(220), 2953(220).	500(3), 517(2), 771(4), 806(3), 827(4), 896(5), 956(2), 985(3), 1081(1), 1149(3), 1187(2), 1316(2), 1346(1), 1457(10), 2736(0), 2865(8), 2923(8), 2950(7).	251(3,w), 262(6,w), 278(0,w), 326(0), 394(0), 497(35), 527(5), 586(0), 607(4,w), 721(0), 766(27,dl.), 798(0), 861(5), 896(34), 957(5,w), 1005(4), 1022(5), 1081(13, w), 1147(10), 1186(3,w), 1286(2), 1303(2), 1340(5), 1360(3),1457(40,w,dl.), 2676(0), 2726(4), 2854(170,w), 2868(190), 2906(100), 2924(150), 2957(230, dl.).

The brightness of the lines was determined visually on a ten-point scale. The degrees of brightness given by Bazhulin were determined with the aid of a microphotometer, so that it was not possible to observe most of the faint lines on the spectrogram obtained. Comparison of the spectra makes clear that the spectrum of the fraction under study contains the lines typical of 1,3-dimethylcyclopentane and trans-1,2-dimethylcyclopentane.

Technical difficulties made it impossible to obtain Raman spectra of the 4th and 5th fractions (95-100 and 100-105°), so that characterization of their composition was limited to determination of boiling point and refractive index. Judging by the refractive index, the fourth fraction (95-100°, n_D^{20} 1.4190) consisted chiefly of a mixture of trans-1,2- and cis-1,2-dimethylcyclopentanes (b.p. 91.9°, n_D^{20} 1.4120 and b.p. 99.2°, n_D^{20} 1.4276, respectively). The constants of the 5th fraction made it possible to postulate that it (b.p. 103.4°, d_4^{20} 0.7669, n_D^{20} 1.4220) consists of an equilibrium mixture of ethylcyclopentane (b.p. 103.4°, d_4^{20} 0.7669 n_D^{20} 1.4197)and methylcyclohexane (b.p. 100.8°, d_4^{20} 0.7692, n_D^{20} 1.4230).

The residue of the first distillations was distilled from a flask with a 20-cm high column. The product distilled in the range of 103-240° (n_D^{20} 1.4426) and contained 6.6% of aromatic hydrocarbons. After they were removed, the product distilled in the range 120-240°, the refractive index was reduced somewhat (n_D^{20} 1.4410), and the specific gravity was d_4^{20} 0.8038. Elementary analysis proved the naphthenic character of the hydrocarbons of this fraction.

0.1022 g. sub.: 0.3199 g CO_2; 0.1312 g H_2O. Found %: C 85.32; H 14.28, 0.1133, 0.1615 g sub.; 13.95 g C_6H_6: Δ t 0.297°, 0.422°. Found: M 140, 143.

The boiling point, specific gravity and refractive index made it possible to postulate the presence in this fraction of methylated or ethylated homologs of cyclohexane.

To determine the yield of the separate components of the reaction, the catalyzate of the fourth experiment was distilled in a column of 25 theoretical plates, Quadruple distillation yielded the fractions given in Table 2.

TABLE 2

Boiling point	Yield of fraction, (g)	n_D^{20}
37-87°	2.26	1.3925
87-93	11.44	1.4110
93-96	1.47	1.4140
96-100	6.19	1.4187
100-103	16.63	1.4220
103-240	6.97	1.4440
Losses	5.98	—

Table 2 shows that the bulk of the isomerization product of methylcyclohexane fell to fractions corresponding to 1,3-, trans- and cis-1,2-dimethyl cyclopentane (2nd and 4th fractions) and ethyl cyclopentane (5th fraction). A smaller quantity fell to the 6th fractions, containing methylated or ethylated derivatives of cyclohexane, and to the first (methane hydrocarbons).

SUMMARY

The isomerization of methylcyclohexane by a natural aluminosilicate catalyst (gumbrin) at 245-250°, was studied. It was shown that under these circumstances, methylcyclohexane undergoes isomerization, by ring contraction, to cyclopentane derivatives. Methane, aromatic and higher methylated or ethylated cyclohexane homologs are produced in smaller quantities.

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ON THE MECHANISM OF INHIBITOR ACTION

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Kashtanov and Ryzhov [1] have studied the inhibitory action of phenol on the process of oxidation of sulfur dioxide in aqueous solution. Reiter's researches had established [2] that insignificant additions of sulfur dioxide to phenol sharply inhibit the oxidation of the latter by atmospheric oxygen. Thus, there is an interrelation between the inhibitory action of phenol on the process of oxidation of sulfur dioxide and of sulfur dioxide on the autooxidation of phenol by atmospheric oxygen. Phenol is a good inhibitor of the oxidation of tin sulfate [3], chloroform [4] and rubber [5].

TABLE 1

Time (minutes)	Percent oxidation of sodium sulfite		
	Pure	In the presence of agerite	In the presence of neozone
5	9.21	3.75	11.25
15	35.52	8.75	28.75
25	84.21	11.25	57.5
35	97.36	16.25	78.75
45	100.00	22.5	96.25
55	—	27.5	97.5
65	—	27.5	100

In this connection it appeared of interest to determine the action of the rubber oxidation inhibitors now in use, neozone and agerite, upon the rate of oxidation of sodium sulfite.

In these experiments, all inhibitors were used in the form of 0.1% solutions.

Table 1 presents comparative data obtained as described by Kashtanov and Ryzhov [1], on the rate of oxidation of sodium sulfite by atmospheric oxygen in presence of neozone and agerite. These data show that both inhibitors seriously affect the oxidation of sodium sulfite.

Aniline and other amines are used as stabilizers for rubber [7]. Aniline is also a good inhibitor when divalent tin and divalent iron [6] are oxidized by benzaldehyde [8].

TABLE 2

Time (minutes)	Percentage oxidation of sodium sulfite				
	Pure	In presence of aniline	In presence of m-toluidine	In presence of o-toluidine	In presence of p-toluidine
5	9.21	7.9	3.7	7.4	20.0
15	35.52	20.7	8.6	17.5	50.0
25	84.21	29.7	17.7	27.7	78.0
35	97.36	34.6	17.7	36.1	85.0
45	100.00	44.5	22.0	40.7	89.0
55	—	51.4	24.48	46.2	90.0
65	—	54.4	24.48	53.7	93.0

We tested aniline and other amines as inhibitors of oxidation of sodium sulfate. The results obtained are presented in Table 2.

TABLE 3

Time (min.)	Percent oxidation of sodium sulfite	
	Pure	In presence of hydroquinone
5	9.21	0.98
15	35.52	1.96
25	84.21	2.94
35	97.36	2.94
45	100	—

As the data in Table 2 show, m-toluidine had the greatest inhibitory effect upon sodium sulfite oxidation; aniline and o-toluidine were of medium effect; and p-toluidine the least

Ivanov [9] refers to hydroquinone as an inhibitor of isopropyl ether oxidation, and Mekhrov [10] as the most powerful inhibitor against oxidation of fish and sea-mammal fats by atmospheric oxygen. Hydroquinone is also an inhibitor of benzaldehyde [11] and hypophosphorous acid oxidation [12]. We established that hydroquinone is a powerful inhibitor of sodium sulfite oxidation (Table 3).

SUMMARY

The sources cited in the literature and the results of additional experiments testify to the wide applicability of inhibitor action. Phenol inhibits the oxidation of sulfur dioxide, tin sulfate, chloroform and rubber. Sulfur dioxide inhibits the oxidation of phenol. Agerite and neozone inhibit oxidation of rubber and sodium sulfite. Aniline and other amines inhibit the oxidation of rubber, divalent tin, divalent iron, benzaldehyde, and sodium sulfite. Hydroquinone inhibits oxidation of isopropyl ether, fish and sea-mammal fats, hypophosphorous acid and sodium sulfite.

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HYDROLYSIS OF UREIDO ACIDS

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One of the intermediary compounds of ureide derivatives are the ureido acids, $HOOC-R-CO-NHCO-NH_2$, which result from the interaction of dibasic acid anhydrides with urea at the melting temperature of the anhydride [1].

The purpose of this work was a study of the hydrolyzability of ureido acids, and in particular, of maleureido, succinureido and phthalureido acids. Results of such investigation ought to help clarify the resin formation process which takes place in aqueous solution upon interaction of ureido acids with formaldehyde.

It was established from the experimental results that at temperatures below 70° in aqueous solution, hydrolysis of ureido acids is almost non-existent. With an increase in temperature, a reaction leading to the formation of dibasic acids and urea was observed for the first stage.

A study of the hydrolysis kinetics indicated that hydrolysis reactions for succinuerido, maleureido and phthalureido acids, found to be bimolecular, correspond, in the case of a dilute solution, to a first order equation. Calculation of the rate constant was carried out according to the first order reaction formula $K = \dfrac{2.303}{\tau} \log \dfrac{C_0}{C}$, where $C < C_0$, in which account was taken of the fact that in the case of ureido acid hydrolysis, the number of milliliters of sodium hydroxide will characterize the reaction of new carboxyl group formation and $V_1 > V_0$.

Hence $\dfrac{V_1 - V_0}{V_0} = \dfrac{\Delta C}{C_0}$ and $\dfrac{C}{C_0} = \dfrac{2V_0 - V_1}{V_0}$. Substituting, we get $K = \dfrac{2.303}{\tau} \log \dfrac{V_0}{2V_0 - V_1}$.

Rate constants, calculated according to this equation, were: for 0.01 N solution of succinuerido acid at 100° = 0.00055; for 0.00977 N solution of maleureido acid at 80° = 0.00162, and at 98° = 0.00277; for 0.01086 N solution of phthalureido acid at 98° = 0.00268.

Hydrolysis of a ureido acid is found to be a gradual process. The urea which is formed in the first stage decomposes further to ammonia and carbon dioxide. For a dilute solution (concentration of 0.01 N), at a temperature of about 80°, the amount of urea decomposing is negligible, and the amount of evolving ammonia is greater than the range of experimental error. In concentrated solutions, for example of maleureido acid, and at 100° and above, the ammonia formed by hydrolysis decreases the total acidity of solution, interacting first with formation of ammonium salt, and second, with maleureido acid molecules which are being formed, giving an acid and intermediate salts.
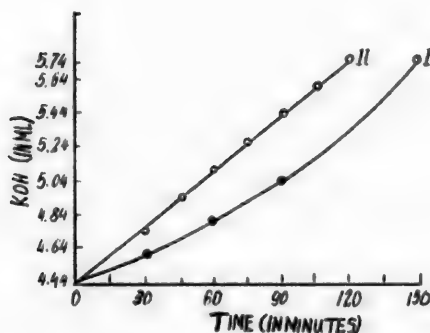

Fig. 1. Relation of hydrolysis rate for 0.00977 N maleureido acid to that of temperature.
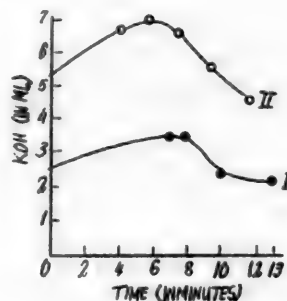
I - 80°, II - 98°.

Fig. 2. Relation of hydrolysis rate of maleureido acid to time

I - 0.05 N solution
II - 0.1 N solution

On the basis of what has been stated above, the shape of the curve which characterizes hydrolysis of maleureido acid at 98° differs from that at 80° (Fig. 1), and the curves characteristic for decomposition of maleureido acid in 0.05 N solution, and more concentrated solutions, pass through a maximum (Fig. 2) upon prolonged heating.

The salts of maleureido acid are more stable to hydrolysis than the free acid. Sodium and potassium salts (0.01 N solutions), are practically unaffected by heating for 150 minutes at 99°. The stability of the salt, however, is determined by the nature of the metal which is substituted for the carboxyl hydrogen. Thus, lithium salts under similar conditions are noticeably hydrolyzed.

This can be explained on the basis of mutual influence of atoms, as well as by variation in volume of the metallic atoms which replace the hydrogen. The larger the atomic volume of an element, the more it will hinder attraction of water molecules, which are necessary for the peptide bond, analogous to break-down of polypeptides [2].

Various ureido acids hydrolyze at various rates. Thus the nature of the radical — the radical of the dibasic acid bound to the —CONH— group — also has an influence upon stability of the peptide bond in molecules of ureido acids.

EXPERIMENTAL

Synthesis of Succinureido Acid. 20 g of succinic anhydride and 12 g of urea were heated on an oil bath at 120° for 30 minutes to complete solidification of the molten mass. The substance, recrystallized from hot water, was dried to constant weight. Yield of acid was quantitative.

Found %: N 17.40, 17.45 (Kjeldahl). $C_5H_8O_4N_2$. Calculated %: N 17.49. Found: Acid number 348.3. Calculated: Acid number 349.7.

Synthesis of Maleureido Acid. 20 g of maleic anhydride and 12 g of urea were heated in a round-bottomed flask at 60° for 45 minutes, with stirring. Having increased temperature to 80°, heating was continued for another 15 minutes until the entire mass had completely solidified. After recrystallizing from hot water, and drying to constant weight, maleureido acid resulted in quantitative yield.

Found %: N 17.60, 17.55. (Kjeldahl). $C_5H_6O_4N_2$. Calculated %: N 17.7. Found: Acid number 353.4, 354.8. Calculated: Acid number 354.

Synthesis of Phthalureido Acid. 26 g of phthalic anhydride and 10.5 g of urea were heated at 120° for 20 minutes to complete solidification of the entire mass. After crystallization and drying, phthalureido acid resulted in quantitative yield.

Found %: N 13.52, 13.60 (Kjeldahl). $C_9H_8O_4N_2$. Calculated %: N 13.45. Found: Acid number 266, 267.5. Calculated: Acid number 268.9.

Hydrolysis Procedure. A flask containing 10 ml of water was placed in a thermostat. After heating the water to the required temperature, a batch of the acid was added and the mixture stirred vigorously to complete dissolution. A sample was then taken for determination of initial acidity, and the stop-watch then started. Acidity determination was carried out with 0.0111 N solution of potassium hydroxide, using phenolphthalein. Results are given in Tables 1-5.

TABLE 1

Relation Between Maleureido Acid Hydrolysis and Temperature   (Acid concentration 0.00977 N)

Duration of experiment (in minutes)	Milliliters of KOH used for neutralization			K	
	70°	80°	98°	80°	98°
0	4.44	4.44	4.44	—	—
30	4.44	4.60	4.74	0.00159	0.00260
45	4.44	—	4.92	—	0.00280
60	4.44	4.82	5.08	0.00163	0.00278
75	4.44	—	5.22	—	0.00276
90	4.44	5.02	5.38	0.00165	0.00278
105	4.44	—	5.58	—	0.00284
120	4.44	—	5.74	—	0.00262
135	4.44	5.74	—	0.00161	—
			Average................	0.00162	0.00277

TABLE 2

Relation Between Maleureido Acid Hydrolysis and Time at 98°

Time (in hours)	Milliliters of KOH (0.08547 N) to neutralize the 0.05 N solution of acid.	Time (in hours)	Milliliters of KOH (0.08547 N) to neutralize the 0.1 N solution of acid.
0	2.65	0	5.3
7	3.4	4	6.6
8	3.55	5.5	6.9
10	2.3	7.5	6.5
13	2.2	9.5	4.5
		11.5	

TABLE 3

Hydrolysis of 0.01 N Solution of the Lithium Salt of Maleureido Acid

Time (in minutes)	0.0111 N KOH (in ml)
15	0
30	0.04
45	0.05
60	0.06
90	0.07
120	0.08
150	0.1

TABLE 4

Hydrolysis of 0.01 N Solution of Succinureido Acid at 100°

Time (in minutes)	0.011 N KOH (in ml)	K
0	4	—
45	4.10	0.00055
60	4.14	0.00057
75	4.16	0.00055
90	4.18	0.00051
120	4.26	0.00056
135	4.30	0.00057
150	4.32	0.00055
	Average	0.00055

TABLE 5

Hydrolysis of 0.01086 N Solution of Phthalureido Acid at 98°

Time (in minutes)	0.011 N KOH (in ml)	K
0	4.9	—
30	5.24	0.00240
45	5.40	0.00239
60	5.6	0.00255
90	6.24	0.0034
	Average........	0.00268

Among the hydrolysis products of maleureido acid which was heated for a prolonged period, were found maleic acid and the ammoniacal salt of maleureido acid. 0.05 N maleureido acid solution, heated for 8 hours, was then extracted repeatedly with ether. From the ether extract a product, m.p. 130°, crystallized out. A sample mixed with known maleic acid did not give depression. The solution, treated with ether, was evaporated to the point of crystallization. After drying, there resulted crystals of the ammoniacal salt of maleureido acid.

Found %: N 24.2 (Kjeldahl). $C_5H_9O_4N_3$. Calculated %: N 24.00.

SUMMARY

1. Hydrolyzability of malerueido acid, its salts, of succinureido and of phthalureido acids, has been investigated.

2. Hydrolysis rate constants for maleureido, succinureido and phthalureido acids have been determined.

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REACTION OF ETHYLENE CHLOROHYDRIN WITH
2,5-DICHLOROANILINE AND ANILINE

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We have previously demonstrated [1] that the reaction of ethylene chlorohydrin with 2,5-dichloroaniline, accompanied by the production of N-ethanol-2,5-dichloroaniline (2,5-dichlorophenylethanolamine) does not proceed as maintained by Krasussky, via a stage in which ethylene oxide is formed, then to react with amine, but by direct exchange of a halide for an amino group. This was confirmed by the fact that ethylene oxide in isolation does not react with 2,5-dichloroaniline.

The present study had the purpose of clarifying whether 2,5-dichloroaniline would react with ethylene oxide at the moment of its production. Toward that end we set up the following experiment. Into an apparatus containing 2,5-dichloroaniline and a solution of caustic soda, we gradually poured ethylene chlorohydrin, which, as is known [2], reacts immediately with caustic soda, producing ethylene oxide; it appeared thereby that the ethylene oxide produced under these conditions of experiment, did not react with 2,5-dichloroaniline and left the reaction zone. This was also confirmed by a control experiment so conducted that the ethylene oxide produced from ethylene chlorohydrin and leaving the   reaction zone, was caught in a trap containing aniline. Monoethanolaniline was accordingly produced in the trap where the ethylene oxide underwent absorption by aniline. But the control experiment also failed to produce N-ethanol-2,5-dichloroaniline. It follows, therefore, that ethylene oxide does not react with 2,5-dichloroaniline at the moment of its formation.

The reaction of ethylene chlorohydrin with aniline was studied in passing in this investigation. It is known that reaction of ethylene chlorohydrin with aniline and its derivatives is usually accomplished by heating these substances, mixing them the while [2-4]. Shorygin, Smirnov and Belov [5,6] describe this process as taking place in the presence of water, which increases the yield of monoethanolaniline (80%). In this procedure, the separation of monoethanolaniline from the reaction mixture is performed in the usual way [2-6].

Unlike the foregoing, Rindfus and Harnack [7] conducted this reaction in presence of soda and obtained monoethanolaniline and diethanolaniline simultaneously, although they did not indicate the yields of these products. Nevertheless, this approach is of definite interest, as it is capable of being used for the synthesis of diethanolaniline and other dialkanolanilines.

Judging by our observations, however, the ethylene chlorohydrin reaction with aniline should preferably be conducted not in the presence of soda, as soda tends to cause hydrolysis of ethylene chlorohydrin into ethylene glycol [2], but in the presence of chalk, caustic soda or lime. When this is done, the experiments show that the reaction proceeds chiefly in the direction of the production of the ethanol derivatives of aniline. *

We obtained analogous results in synthesizing diethanolaniline. In this instance we used a 2.2 : 1 ratio of initial ethylene chlorohydrin and aniline, with the result that when reacted in the presence of chalk the diethanolaniline yield was 79.22% of theory, and 83.04% when conducted in the presence of caustic soda.

In addition, for purposes of comparison we attempted to obtain diethanolaniline (without use of alkali and chalk) by heating 2.2 mole of ethylene chlorohydrin with 1 mole of aniline in the presence of 10 ml water. It turned out, however, that in this instance the reaction proceeded mainly to the production of monoethanolaniline. Diethanolaniline was produced in but an insignificant quantity, and we did not succeed in isolating it from the reaction mixture in pure form.

As far as the mechanism of the reaction of ethylene chlorohydrin and aniline are concerned, when this process occurs in the presence of chalk and alkalis, which readily convert ethylene chlorohydrin into ethylene oxide [2,8], the reaction probably does proceed chiefly through the stage of oxide formation and its subsequent reaction with aniline. However, this does not contradict Krasussky's rule [9], which established in terms of the reactions of isomeric a -monochlorohydrins that under ordinary circumstances, i.e., in the absence of alkalis, "the formation of a -aminoalcohols from a-monochlorohydrins proceeds through a -oxides", constituting intermediate products in the reaction of ammonia and the amines with a -monochlorohydrins.

Thus, for example, by heating 1 mole of ethylene chlorohydrin with 2 moles of aniline in the presence of chalk, we obtained an 83% yield of monoethanolaniline.

However, it is not impossible that the production of monoethanolaniline and diethanolaniline from aniline and ethylene chlorohydrin may also take place to some degree by direct exchange of a halide for an amino group, as, for example, in the derivation of N-ethanol-2,5-dichloroaniline from 2,5-dichloroaniline and ethylene chlorohydrin [1].

EXPERIMENTAL

Effort to obtain N-ethanol-2,5-dichloroaniline from 2,5-dichloroaniline and ethylene oxide at the moment of its formation. 162 g 2,5-dichloroaniline, 40 g caustic soda and 100 ml water were heated to boiling, stirred constantly, and 80.5 g ethylene chlorohydrin was then poured gradually into the mixture. N-Ethanol-2,5-dichloroaniline was not obtained. The results of this experiment show that ethylene oxide at the moment of its formation does not react with 2,5-dichloroaniline, but does react with aniline (280 g) in the trap at 100 g, giving monoethanolaniline. The monoethanolaniline thus formed was separated from the aniline by fractionation in vacuum. The aniline was driven off in a column. The remainder was redistilled from a Claisen retort. When this was done, the monoethanolaniline fraction (25.2 g) was collected within 147-148°/8 mm:

d_{20}^{20} 1.0942, n_D^{20} 1.5780 [10].
Found %: N 10.2. $C_8H_{11}ON$. Calculated %: N 10.21.

Production of monoethanolaniline and diethanolaniline from aniline and ethylene chlorohydrin in the presence of caustic soda. The ethylene chlorohydrin and aniline were placed in a three-necked flask provided with a stirrer and a reflux condenser, and heated to 100°. A solution of caustic soda was then gradually added to the mixture in the course of 7 or 8 hours through a dropping funnel. The reaction was conducted in an oil bath whose temperature was maintained at between 100 and 110° throughout the entire process.

Data on the Production of Mono- and Diethanolaniline

Experiment No.	Charge (g)								
	Aniline	Ethylene chlorohydrin	Chalk/water (ml)	NaOH/water (ml)	monoethanolaniline*			diethanolaniline	
					yield (in %)	b.p./ 4-5 mm	n_D^{20}	yield (in %)	m. p.
1	186	80.5	—	40/150	78.72	135−145°	1.5805	—	—
2	93	177.1	—	88/330	—	—	—	83.04	51−52°**
3	232.5	80.5	62.5/100	—	83	134−138	1.5800	—	—
4	93	177.1	120/100	—	—	—	—	79.22	53−55

* Constants of product obtained correspond to data in literature [10].
** After recrystallization from benzene the diethanolaniline consists of white needles of m.p. 57-58° [11]. Found %: N 7.74. $C_{10}H_{15}O_2N$. Calculated %: N 7.73.

At the end of the process the reaction products were separated off from the water layer and fractionated in vacuum. The results of distillation of monoethanolaniline are given in the table (Experiment 1). Diethanolaniline was collected between 185 and 195° at 3 mm; upon standing it congealed into a yellow crystalline mass (Experiment 2).

Production of monoethanolaniline and diethanolaniline from aniline and ethylene chlorohydrin in the presence of chalk. Ethylene chlorohydrin from a dropping funnel was gradually added in 2 hours to a mixture of aniline, chalk and water heated to 80-100°, stirring being constant. The mixture was then heated to boiling and mixed for another 8 to 14 hours.

When monoethanolaniline was produced (Table, Experiment 3), the product was suction filtered out of the mineral residue at the end of the reaction, separated from the water layer and fractionated in a vacuum.

When diethanolaniline was produced (Experiment 4), the reaction mass was diluted with 200 ml water and 300 ml benzene for ease of filtration. Upon fractionation, the diethanolaniline fraction was collected between 165 and 169°/ 1.5 mm. When allowed to stand, the product formed a yellow crystalline mass.

SUMMARY

This study confirmed the opinion we had advanced previously that the formation of N-ethanol-2,5-dichloroaniline from 2,5-dichloroaniline and ethylene chlorohydrin proceeds not by Krasussky's rule, but by direct exchange of a halide for an amino group. At the same time is was shown that the formation of ethanol derivatives of aniline from aniline and ethylene chlorohydrin in the presence of chalk and caustic soda takes place for the most part through a stage in which ethylene oxide is formed, which then reacts with amino, i.e., as stated by Krasussky.

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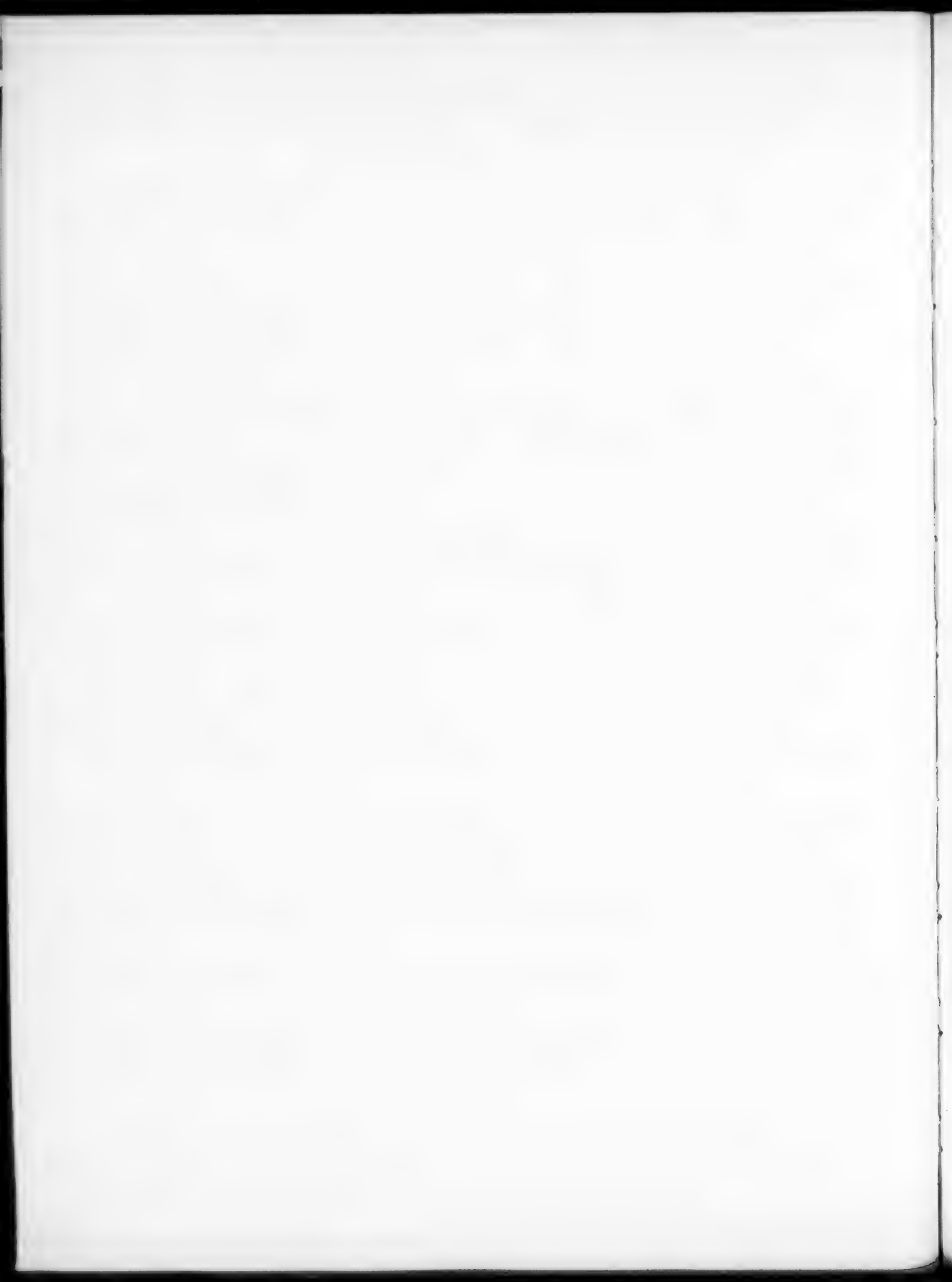
TRANSETHERIFICATION OF DIALKYLAMINOMETHYLAKYL ETHERS
AND DIALKYLAMINOMETHYLALKYL SULFIDES

R. A. Lapina and K. G. Mizuch

Having proved the ability of dialkylaminomethylalkyl ether mixtures (I) [1] to exchange alkoxyl groups at elevated temperatures, we regarded it as of interest to study this reaction in mixtures of ethers (I) with their sulfide analogs the dialkylaminomethylalkyl sulfides $\underset{R}{\overset{R}{>}}NCH_2SR'$ (II). The work of Prilezhaeva, Shapiro and Shostakovsky [2], demonstrating the ability of the a,β-dialkoxydiethylsulfides, with monothioacetal structure, to take on symmetry with heating or in presence of acids, with the formation of equimolecular quantities of dialkylacetals and dialkoxydiethyl mercaptals, made it possible to postulate the transetherification of mixtures of ethers (I) and (II) sulfides. These sulfides (II) were first synthesized by McLeod and Robinson [3] by reacting dialkylamine, mercaptan and an aqueous solution of formaldehyde, but received no further study by anyone. The only chemical property of these compounds noted was the fact that the sulfides were more stable to hydrolysis than the ethers (I). While diethylaminomethyl ethyl ether decomposes to a secondary amine, formaldehyde and alcohol, when merely shaken with cold water, diethylaminomethylisopropyl sulfide hydrolyzes slowly only under the action of hot water.

We obtained the initial dialkylaminomethylalkyl sulfides by heating the ethers (I) with mercaptans in conditions analogous to those we had described earlier for reacting ethers (I) with alcohols.

This method permitted the reaction to proceed in a homogenous medium without a solvent, which was particularly convenient in working with high-molecular mercaptans, virtually insoluble in water. When diethylaminomethyl ethyl ether (III) was heated with n-octyl- and n-decylmercaptans, we obtained diethylaminomethyl-n-octyl sulfide (IV) and diethylaminomethyl-n-decyl sulfide (V), in yields, respectively, of 91 and 80% of the theoretical.

The synthesized dialkylaminomethylalkyl sulfides (IV) and (V) were employed in transetherification reactions with ethers (I).

An equimolecular mixture of piperidinomethyl ethyl ether and (IV) was heated in a sealed ampoule for 40 hours at 140°. After fractionated vacuum distillation, the dark, free-flowing liquid resulting from the reaction gave both expected reaction products: diethylaminomethyl ethyl ether (III) (yield 34.6% of theoretical) and piperidinomethyl-n-octyl sulfide (VI) (yield 37.6% of theoretical)

$$C_5H_{10}NCH_2OC_2H_5 + (C_2H_5)_2NCH_2SC_8H_{17} \rightarrow C_5H_{10}NCH_2SC_8H_{17} + (C_2H_5)_2NCH_2OC_2H_5.$$
$$\qquad\text{(IV)} \qquad\qquad\qquad\qquad\qquad\text{(VI)} \qquad\qquad\qquad\text{(III)}$$

Heating of a mixture of diethylaminomethyl-n-decyl sulfide (V) and piperidinomethyl ethyl ether under the same conditions gave piperidinomethyl-n-decyl sulfide (VII) (yield 30% of theoretical) and ether (III).

Thus, it may be taken as proved that the heating of a mixture of dialkylaminomethyl alkyl ether and dialkylaminomethylalkyl sulfide causes exchange of alkoxyl and alkyl sulfide groups.

All the sulfides described (IV, V, VI and VII) were here produced for the first time. They are free-flowing, colorless liquids with strong and unpleasant odor, undergo vacuum distillation without decomposition, are readily soluble in organic solvents and virtually insoluble in water.

EXPERIMENTAL

Diethylaminomethyl-n-octyl sulfide (IV). A mixture of 29.2 g n-octyl mercaptan (0.2 mole) and 28.8 g ether (III) (0.22 mole) was heated to 130° in a three-necked bottle, equipped with stirrer, thermometer and descending condenser. Ethyl alcohol began to be given off at that temperature. Within an hour and a half the temperature of the reaction mass reached 170°, when distillation ended. The total amount of ethyl alcohol given off was 7.1 g, containing 0.7% of nitrogenous compounds (recalculated as nitrogen).

Fractionated vacuum distillation of the reaction mass gave 42.4 g of sulfide (IV) (91.6% of the theoretical).

B.p. 134°/6 mm, d_4^{20} 0.8678, n_D^{20} 1.4692, MR_D 74.30; calculated 83.54.

4.820 mg substance: 11.968 mg CO_2; 5.410 mg H_2O. 4.840 mg substance 11.992 mg CO_2; 5.506 mg H_2O. 4.468 mg substance: 1.908 ml 0.02 N $Na_2S_2O_3$. 0.4778, 0.4750 g substance: 19.90, 19.80 ml 0.1N HCl. Found %: C 67.76, 67.61; H 12.56, 12.72; S 13.68; N 5.83, 5.84. $C_{13}H_{29}NS$. Calculated %: C 67.46; H 12.63; S 13.86; N 6.05.

Diethylaminomethyl-n-decyl sulfide (V). A mixture of 10.45 g n-decylmercaptan and 3 g (III) was heated until ethyl alcohol began to be given off; at that temperature (125-128°) another 5.7 g (III) was added in the course of an hour. It was then heated for two hours at 140-145° until distillation ceased (1.8 g; 1.0% content nitrogen compounds). Fractional vacuum distillation of the reaction mixture gave 12.4 g (V) (79.7% of the theoretical).

B.p. 167-169° at 5 mm, d_4^{20} 0.8672, n_D^{20} 1.4683, MR_D 83.21; calc. 83.54.

7.554 mg substance: 19.298 mg CO_2; 8.582 mg H_2O; 2.700 mg SO_4. 6.850 mg substance: 17.495 mg CO_2; 7.808 mg H_2O; 2.500 mg SO_4. 0.2478, 0.2708 g substance: 9.27, 10.13 ml 0.1N HCl. Found %: C 69.71, 69.70; H 12.71, 12.75; S 11.93, 12.18; N 5.24, 5.22. $C_{15}H_{33}NS$. Calculated %: C 69.42; H 12.82; S 12.36; N 5.40.

Transetherification of diethylaminomethyl-n-octyl sulfide (IV) and piperidinomethyl ethyl ether. A mixture consisting of 17.32 g sulfide (IV) and 10.72 g piperidinomethyl ethyl ether was heated in a sealed ampoule at 140° (in xylol vapor) for 40 hours. The reaction mass darkened noticeably. Two main fractions were obtained after fractional vacuum distillation: 1st, b.p. 57-62° at 20 mm, 6.1 g; 2nd, b.p. 156-157° at 8 mm, 13.5 g. Distillation of the 1st fraction under normal pressure in a laboratory rectification column gave 3.4 g ether (III) (34.6% of theoretical) with b.p. 132-133°. According to the literature on (III) its b.p. is 132-134° [4].

Found %: N 10.63, 10.54. $C_7H_{17}ON$. Calculated %: N 10.68.

Vacuum redistillation of the 2nd fraction gave 6.85 g of sulfide (VI) (37.6% of the theoretical).

B.p. 159-160° at 6 mm, n_D^{20} 1.4887, d_4^{20} 0.9105, MR_D 77.12; calc. 76.72.

5.472 mg substance: 13.820 mg CO_2; 5.882 mg H_2O. 4.136 mg substance: 10.432 mg CO_2; 4.468 mg H_2O. 3.880 mg substance: 1.583 ml 0.02 N $Na_2S_2O_3$. 3.451 ml substance: 1.421 ml 0.02 N $Na_2S_2O_3$. Found %: C 68.97, 68.82; H 12.03, 12.09; S 13.08, 13.20. $C_{14}H_{29}NS$. Calculated %: C 69.06; H 12.01; S 13.17.

Transetherification of diethylaminomethyl-n-decyl sulfide (V) and piperidinomethyl ethyl ether. A mixture of 8 g sulfide (V) and 4.4 g piperidinomethyl ethyl ether was heated and processed as above.

The result of fractional vacuum distillation was the recovery of 0.7 g ether (III) and 2.5 g (30%) sulfide (VII).

B.p. 150-152° at 3 mm, n_D^{20} 1.4831.

5.360 mg substance: 13.908 mg CO_2; 5.889 mg H_2O. 5.446 mg substance: 14.088 mg CO_2; 5.978 mg H_2O. 3.815 mg substance: 1.421 ml 0.02 N $Na_2S_2O_3$. Found %: C 70.81, 70.59; H 12.30, 12.28; S 11.94. $C_{16}H_{33}NS$. Calculated %: C 70.78; H 12.25; S 11.81.

SUMMARY

1. The production of dialkylaminomethylalkyl sulfides by reacting dialkylaminomethyl alkyl ethers with mercaptans was demonstrated to be possible.

2. It was shown that heating of a mixture of dialkylaminomethyl alkyl ethers and dialkylaminomethylalkyl sulfides resulted in the exchange of alkoxyl and sulfhydryl groups.

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EFFECTS OF VARIOUS CATALYSTS UPON THE DIRECTION AND
RATE OF BROMINATION OF AROMATIC COMPOUNDS

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It is known that chlorination and bromination of benzene, depending upon conditions of the reaction, proceeds in one of two directions. In the presence of ferric or aluminum halide, and many other catalysts, substitution of hydrogen atoms takes place; in light, or in the presence of sodium carbonate, halogen addition takes place. Replacement of hydrogens on carbon atoms of the benzene ring for benzene homologs is promoted by the same catalysts as for benzene itself; in light and with heating, as well as in the presence of phosphorous halides, substitution in the side chain predominates [1].

After comparing a number of factors, the conclusion can be reached that the benzene molecule itself enters more readily into an addition reaction than into a substitution reaction. This was definitely proved for the chlorination of benzene by N. N. Vorozhtsov [2]. For the homologs of benzene, substitution of hydrogen in the side chains proceeds most readily. Light and heat are the physical factors which on the whole cause weakening and rupture of the bonds, under which conditions those bonds which are weak rupture most readily. Catalysts which promote substitution in the benzene ring are substances of the electron-accepting type. They, or their complexes with other components of the reacting mixtures (for example with halogens, organohalogen compounds, etc.) add in a complex way to carbon of the benzene ring, weakening the carbon-hydrogen bond to such an extent that this bond is more readily ruptured than any other bonds in the molecule. The effect of sodium carbonate upon the direction of chlorination and bromination of benzene can be explained as follows: upon reaction of halogen with benzene, the addition reaction occurs more readily, but substitution of hydrogen can also proceed to a small extent; the evolving HCl or HBr reacts with their proton as an electron-accepting catalyst, accelerating substitution; sodium carbonate, however, neutralizes the hydrogen halide [3]. In similar fashion should act water, which physically removes hydrogen halide from the area of reaction. Upon halogenation of benzene homologs, water and sodium carbonate should promote substitution in the side chain. Hence it might also be expected that in the presence of water and other substances, which promote addition in the benzene ring and substitution in the side chains of homologs, that the halogenation reaction would proceed more slowly. As far as the standard catalysts are concerned, the more a given catalyst accelerates the reaction, the more substitution in the ring should predominate over other directions of chlorination and bromination.

The main purpose of the present work was to reexamine these positions.

Benzene bromination experiments carried out without additives, as well as in the presence of dry hydrogen bromide and water, have indicated that HBr accelerates the reaction noticeably, and that water decelerates the reaction. Acetic acid, which can bind HBr, converting it into a complex, inhibits the bromination reaction somewhat, but does not remove the HBr from the sphere of reaction because it mixes with benzene.

Determination of the benzene bromination rate at room temperature was carried out with a large number of catalysts of positive and negative actions. For the experiments, simple materials were taken for the most part, which converted into bromide in the reaction process. The average temperature was $18°$, with the same fluctuation in all experiments.

The highest acceleration of bromination was observed with the action of iron and of zinc. Bi, Cu, Hg, Pb, Mg, Cd, Te, Mo, Sn were not so effective. I, Co, Al, Sb, Mn, Ni displayed even less activity. P, As, S, Se were found to be very weak catalysts. Nitro compounds inhibited benzene bromination somewhat; iodobenzene accelerated bromination of benzene noticeably.

Toluene reacted more rapidly than benzene. Arrangement of catalysts in order of their power of action approximated on the whole that observed with benzene. Fe and Zn accelerated bromination the most; HBr accelerated somewhat, but water did not inhibit. Chlorobenzene brominated more slowly with a majority of the catalysts than did benzene, but with tellurium, brominated more rapidly. Nitrobenzene reacted very slowly, while a stronger accelerating action was observed for Bi and for Zn at the beginning of the reaction; however, over a longer time, interaction was accelerated more significantly by Al, S, Fe.

In experiments with simple compounds, measurements of reaction rates were complicated by the fact that such compounds converted into bromides not at a uniformly rapid rate. This apparently explains the variation in course of the process. At times bromination proceeded quite uniformly, and at times with a sharp change in rate one way or the other. Thus, with mercury, only 2.7% bromine was used within the first day, and 94.6% after 50 days; with copper the figures were, respectively, 81.5 and 84%, and for iodobenzene, 39.3 and 43.8%.

More clear-cut results in the sense of comparison of the activities of catalysts should be given from experiments with commerical bromides. Such an investigation was carried out by the authors for only a few catalysts, and for each catalyst only one experiment was carried out. Bromination of benzene was carried out in a thermostat (temperature 45°). The catalysts were arranged by strength of action in the following order: $FeBr_3 > AlBr_3 > ZnBr_2 > IBr_3 > SbBr_3 > AsBr_3 > CuBr_2 > S_2Br_2 > PBr_5$. Here of special interest was the low activity of zinc and of copper bromides. This is related, it is thought, to the fact that other bromides were in solution, while $ZnBr_2$ and $CuBr_2$, as separate experiments indicated, are insoluble in benzene. Hence, in this case the catalysis possessed a heterogeneous character, and the reaction rate depended to a great extent upon powdering of the catalyst. The bromides were simply ground to a powder, and in experiments with metallic zinc and copper, the latter were taken in the finely powdered state.

Zinc in the form of dust can be recommended for practical use in the bromination of benzene in organic synthesis laboratories. In a majority of the manuals for synthesis of organic compounds, benzene bromination in the presence of iron is proposed. Ortner and Reichel [4] recommend pyridine for the catalyst. Having noticed a high activity for zinc, the authors carried out the reaction under identical conditions with all three catalysts Fe and Zn gave the same quantitative yield of C_6H_5Br with negligible amounts of dibromobenzene; however, with pyridine there resulted 68.4% C_6H_5Br and 8% $C_6H_4Br_2$. Zinc had the added advantage over iron that $ZnBr_2$ is colorless and does not hydrolyze readily; these facts facilitated subsequent treatment of the reaction mixture. Experiments with different amounts of zinc dust indicated that to obtain good results it is sufficient to take 0.005 to 0.01 g at. wt. of zinc per mole of bromide.

Results of determination of reaction products upon bromination of benzene and toluene with different additives, confirmed, on the whole, the initial hypotheses. Those catalysts which accelerate bromination promote substitution of hydrogen on the benzene ring, and, as a rule, the percentage of bromobenzene or of bromotoluenes in the bromination product is higher, the stronger the catalyst. On the whole, however, there is not observed here a strict parallelism. Additives which inhibit the reaction, in the case of benzene, direct to a considerable degree toward addition, and with toluene, in the direction of substitution in the methyl group.

EXPERIMENTAL

I. Determination of Benzene Bromination Rate in the Presence of HBr, H_2O, CH_3COOH. A mixture of benzene and bromine in the ratio of 0.02 mole bromine to 1 mole of benzene was divided into 5 portions. One portion was left as a control, gaseous HBr was passed into a second portion to a concentration of 0.05 mole per mole of Br_2, in a third portion HBr was dissolved to a content of 0.1 mole per mole of Br_2, to a fourth portion was added H_2O, and to the 5th portion was added CH_3COOH of the same molecular concentration. All solutions were left to stand in the dark at room temperature. Samples were removed from each, which, after addition of KI, were titrated with sodium thiosulfate. Results are given in Table 1.

TABLE 1

Bromination of Benzene in the Presence of HBr and H_2O

Catalyst	Amount of reacted bromine (in %) with prolonged period for experiment.									
	3 days	8 days	18 days	38 days	5 mo.	13 mo.	16 mo.	17 mo.	18 mo.	22 mo.
Without catalyst	2.6	5.7	7	13.3	25.7	28.4	32.5	39.5	39.5	100
HBr (0.05 mole)	—	5.3	8	16.7	—	41.1	42.9	—	—	—
HBr (0.1 mole)	2.7	10.8	11.2	18.8	31	55.3	57.9	65.8	100	—
H_2O (0.1 mole)	4.2	4.6	7.4	7.4	7.9	8.5	10.6	12.7	—	55.8
CH_3COOH (0.1 mole)	5	7.4	8.7	10.1	15	16.3	56.8	58	—	—

100% bromine was used with water for 30 months, and with CH_3COOH for 28 months.

II. Determination of Bromination Rate of Aromatic Compounds in the Presence of Various Catalysts. A mixture of benzene with bromine in the molecular ratio 50 : 1 was divided into portions, to which were added positive and negative catalysts in the amount of 0.01 mole per mole of bromine. All mixtures were left at room temperature. From them aliquots were taken in which unreacted bromine was determined iodometrically. The data obtained are given in Tables 2 and 3.

Toluene (Table 4), chlorobenzene (Table 5) and nitrobenzene (Table 6) were treated under similar conditions.

III. Bromination of Benzene In the Presence of Bromides of Certain Elements. Benzene and bromine were taken in the amounts of 35 and 10.1 ml , i.e., in the molecular ratio of 2 : 1, catalyst in the amount of 0.01 mole per mole of bromine. Reaction was carried out at 45° for 10 hours. Constancy of temperature was maintained within 0.2° by a thermostat regulated by a mercury-toluene regulator. After completion of the experiment, unreacted bromine was removed by shaking with a 10% solution of NaOH, and the mixture washed several times with distilled water, dried with $CaCl_2$ and fractionated twice, the second time with a dephlegmator. As a result the mixture was sharply divided into two fractions: 80-83° (benzene) and 155-157° (bromobenzene). The residue in the flask was taken to be a mixture of dibromobenzenes. Since losses are unavoidable during treatment of the reaction mixture, an experiment was therefore carried out with a mixture of 10 ml of C_6H_6 and 20 ml of C_6H_5Br without catalyst.

After washing the above-mentioned mixture with alkali and water, drying with $CaCl_2$ and two fractionations, there resulted 18 ml of bromobenzene, i.e., losses amounted to 10%. The results are given in Table 7.

IV. Effects of Temperature and Quantity of Catalyst on the Bromination Rate of Benzene in the Presence of Zinc. The resulting data are given in Tables 8 and 9.

V. Some Preliminary Experiments on Bromination of Aromatic Compounds with Various Catalysts. 1) 22 ml (0.25 mole) of C_6H_6, 10 ml (0.2 mole) of bromine and 0.09 gram at. wt. of Fe powder. Reaction was carried out with heat on a water bath at 40-45°; 31 g of bromobenzene resulted, i.e., about 100% of theoretical yield, with traces of dibromobenzenes.

2) The same quantities of reactants, and experimental conditions, were used, but in place of iron, zinc dust was used. Yield of C_6H_5Br was theoretical.

3) The same, with pyridine as a catalyst. Yield of bromobenzene was 68.4% of theory, p-dibromobenzene was 8%.

4) The same, with C_6H_5I catalyst: yield was 40% for C_6H_5Br, and 6.9% of p-$C_6H_4Br_2$.

5) Same without catalyst: yield of C_6H_5Br 31%.

6) 26.5 ml (0.25 mole) of $C_6H_5CH_3$, 10 ml of Br_2 were taken. Reaction time was 5 hours. Yield (in %) of bromotoluene was 88, of benzyl bromide, 12.

7) The same, with 0.57 g (0.09 g at. wt.) of zinc, reaction time 1 hour, without heating. 16.6 g (48%) of bromotoluene resulted. $C_6H_5CH_2Br$ was not found.

8) The same, with 79.5 ml of water, reaction time about 5 hours at room temperature. After two fractionations with dephlegmator, 14.4 g of bromotoluenes were obtained, benzyl bromide amounting to 2.7 g.

9) 25.5 ml (0.25 mole) of C_6H_5Cl was taken, 10 ml Br_2 and 0.58 g Zn. Time was 12 hours at 40-50°. Yield of chlorobenzenes mixture was 4.3 g (11.2%).

10) The same, with Fe (0.5 g) catalyst, 1 hour without heating. 19.1 g (50%) resulted.

11) 26 ml. (0.25 mole) $C_6H_5NO_2$, 10 ml of Br_2 and 0.5 g of Fe were taken; time was 30 hours at 50-60°. 0.65 g (1.6%) $C_6H_4BrNO_2$ resulted.

12) The same, with catalyst, S. Same conditions. 0.74 g (1.8%) $C_6H_4BrNO_2$ resulted.

VI. A Study of the Influence of Catalysts Upon the Direction of the Reaction.
1) Experiments with Prolonged Bromination of Benzene. Reaction was carried out at room temperature. The molecular ratio of C_6H_6 : Br_2 : catalyst = 50 : 1 : 0.01. The reaction mixture was treated with water, NaOH solution, and again washed with water. The solution was then dried with $CaCl_2$, the benzene distilled off, and then the C_6H_5Br distilled with steam.

The residue after distilling out the C_6H_5Br should have been, according to the literature data, hexabromocyclohexane; HBr was evolved when the former was heated. The data obtained are given in Table 10.

2) Bromination Products of Toluene. The molecular ratio of $C_6H_5CH_3$: Br_2 : catalyst = 50 : 1 : 0.01. Room temperature. Reaction was carried to complete utilization of bromine. The mixture was treated as before, but with direct distillation, without redistillation with steam. The 180-200° fraction, which was found to be a mixture of bromotoluenes and benzyl bromide, was boiled for 40 minutes with an alcoholic solution of KOH, and then diluted with water. The bromotoluenes were extracted with ether, and $AgNO_3$ solution added to an aqueous solution acidified with nitric acid.

The AgBr precipitate was washed, dried on a glass filter at 100° for 5 hours, and weighed. $C_6H_5CH_2Br$ was calculated, and by difference, the amount of $CH_3C_6H_4Br$ was determined. Experimental results are given in Table 11.

TABLE 2
Bromination of Benzene (1st series of experiments)

Duration of experiment	Without catalyst	Quantity of reacted bromine (in %) with catalyst												
		Cu	Mg	Zn	Pb	S	Se	I_2	Fe	H_2O	$C_2H_4O_2$	$C_6H_5NO_2$	$C_6H_4(NO_2)_2$	C_6H_5I
1 hr.	–	79.3	–	85	61.1	–	–	–	88.2	–	–	–	2	–
6 hrs.	–	81.5	58.5	85.7	61.1	–	6	–	89.5	–	–	–	2.56	39.3
1 day	–	81.5	58.5	89.2	61.1	–	6	–	92.1	0	0	–	2.56	39.3
20 days	1.3	83.1	59.4	100	62.3	0.7	–	10	100	0	0	0.7	2.56	40
2 mo.	1.6	83.4	59.8	–	65.3	4.4	6	25.9	–	1.3	2.3	2.3	4.4	41.9
4 mo.	6.7	84	61.7	–	66.8	9.3	7.4	44.9	–	6.1	8.7	8.7	6.8	43.8
7 mo.	9.0	85	62.7	–	71.6	9.7	9	58	–	9.3	13.8	13.8	6.8	45.7

TABLE 3
Bromination of Benzene (2nd series of experiments)

Duration of experiment	Without catalyst	Quantity of reacted bromine (in %) with catalyst												
		Cd	Hg	Al	Sn	P	As	Sb	Bi	Mo	Te	Mn	Co	Ni	$C_6H_2(NO_2)_3OH$
2 hrs.	–	–	1.8	4	–	11.4	8.1	8.1	10	3.2	7.8	0.5	3.2	2.3	–
1 day	1.8	6.4	2.7	4	10	11.4	8.1	8.1	18.2	5.5	8.1	2.8	3.7	3.7	1.0
4 days	1.8	20.5	20	15.5	11.4	–	10	10	38.7	12.7	15.0	4.0	5.5	3.7	1.8
25 days	2.3	54.6	76.4	21	12.8	11.4	10	10	92.8	46.4	46	8.1	9.6	8.2	3.7
50 days	3.7	70	94.6	21	13.2	12.7	11	11	97.8	51.4	58.7	14.6	16	9.6	3.7
4 mo.	5.5	82.8	100	21	17.8	15	15	20	100	63.7	100	25.5	42.8	15.5	–
7 mo.	7.3	86	–	23.2	–	18.2	15	33.7	–	71.9	–	30.5	51.9	19.6	–
14 mo.	8.7	100	–	46.7	72.3	24.1	18.7	49.1	–	80	–	46	59.1	24.1	3.7

TABLE 5
Bromination of Chlorobenzene

Duration of experiment	Without catalyst	Quantity of reacted bromine (in %) with catalyst								
		Mg	Zn	Hg	Al	Bi	Te	S	I	HBr
30 min.	0	1.7	3.3	2.8	1.1	2.8	3.3	1.7	0	2.2
1 hr.	–	–	3.3	2.8	1.1	2.8	10.4	–	0	–
7 hrs.	0.7	1.7	7.2	–	2.2	6.1	83.1	2.8	0	2.2
1 day	1.1	1.7	7.2	2.8	2.2	8.2	89.6	2.8	0	2.8
8 days	1.7	3.3	22.4	7.2	4.4	34.4	100	6.2	0.7	3.9
30 days	1.7	3.3	34.4	10	5	48.6	–	10	5.5	5.0
9 mo.	5.5	6.1	82.6	31.4	14	69.4	–	41	42.8	7.7

T A B L E 4
Bromination of Toluene

Duration of experiment	Without catalyst	Quantity of reacted bromine (in %) with catalyst																	
		Cu	Mg	Zn	Cd	Hg	Al	Sn	Pb	Sb	Bi	S	Te	I	Fe	H_2O	HBr	C_6H_5I	$C_6H_4(NO_2)_2$
30 minutes	0	0	0	2.9	1.8	1.7	1.7	0.9	0.6	5.7	0	0	0	0	2.9	0	0	0	0
1 hour	0	–	2.9	32	5.8	8	–	–	–	–	14.3	2.3	1.2	1.7	3.2	0	0	0	0
2 hours	0	9.2	–	70	–	–	17.7	22.9	13.2	15.5	72	–	10.9	–	–	0	18.3	1.8	1.8
5 hours	2.9	26.3	40.3	80.6	4.6	76.6	27.5	33.8	28	18.9	–	24.6	40.6	42.3	100	8	21.2	8.6	5.8
9 hours	–	–	–	100	63.8	100	29.2	55.5	–	–	100	–	68.6	–	–	8	–	9.6	–
1 day	14.9	26.3	61.2	–	89.2	–	42.9	94.9	40	46.3	–	45.8	98.9	77.2	–	14.8	33.2	25.8	14.9
3 days	25.8	45.8	62.3	–	98.9	–	66.9	100	52.3	74.9	–	61.2	100	88	–	25.8	44.5	34	26.9
4 days	42.9	60.6	63.5	–	100	–	89.9	–	57.2	82.9	–	67.6	–	88.8	–	42.9	61.8	61.8	42.9
10 days	82.3	94.3	91.5	–	–	–	100	–	84.6	96.6	–	91.5	–	–	–	87.2	100	100	81.8
11 days	84.6	98.3	100	–	–	–	–	–	94.3	100	–	97.2	–	–	–	88.6	–	–	–
12 days	89.2	100	–	–	–	–	–	–	100	–	–	100	–	88.8	–	89.2	–	–	–
13 days	100	–	–	–	–	–	–	–	–	–	–	–	–	–	–	100	–	–	–

TABLE 6
Bromination of Nitrobenzene

Duration of experiment	Without catalyst	Quantity of reacted bromine (in %) with catalyst									
		Mg	Zn	Hg	Al	Pb	Bi	S	Te	I	HBr
30 min.	0	1.7	4.6	1.7	1.2	0.6	6.2	2.3	2.3	0	0.6
9 hrs.	0	1.7	4.6	1.7	1.2	—	6.2	2.3	5.7	—	0.6
1 day	0	3.5	4.6	3.5	1.2	0.6	8	2.9	10.3	0	2.3
3 days	0.6	4	6.2	5.7	3.5	—	9.7	3.5	16.2	0	4
45 days	4	4	8	9.7	6.9	0.6	10.3	13.1	22.2	6.2	4
3 mo.	4	6.9	13.1	11.4	13.1	5.7	13.7	19.9	24.5	8.4	4
11 mo.	5.7	13.1	16	16.2	35.3	9.7	16.2	31.3	27.3	12	5.7

TABLE 7
Yields of Bromobenzene and Dibromobenzene in the Presence of Bromides of Various Elements

Reaction products	Catalysts and their weights (in g)									
	—	$CuBr_2$ 0.44	$ZnBr_3$ 0.45	$AlBr_3$ 0.53	PBr_3 0.86	$AsBr_3$ 0.63	$SbBr_3$ 0.73	S_2Br_2 0.45	IBr_3 0.73	$FeBr_3$ 0.59
C_6H_5Br (in g)	2.27	3.67	14.8	18.65	2.2	3.98	4.94	3.64	9.29	23.51
C_6H_5Br (in %)	7.2	11.6	47.1	56.2	7.1	12.6	15.7	11.5	29.5	74.9
$C_6H_4Br_2$ (in %)	—	—	2.7	—	—	—	—	—	—	3.76

TABLE 8
Effect of Temperature Upon the Benzene Bromination Rate (0.01 g at. wt. Zn per mole of Br_2)

Temp.	Quantity of reacted bromine (in %) for duration of experiment											
	30 min.	2 hrs.	6 hrs.	18 hrs.	2 days	4 days	5 days	6 days	7 days	8 days	10 days	12 days
11-12°	3.8	6.3	10.9	17.2	30	42.3	49	54	59	61	—	62.4
about 18°	3.8	8	15.1	28	46.9	67.8	71.8	76.6	82.5	87	—	100
24-25°	3.8	9.3	24.7	36.8	58.1	75.4	83.2	86.6	92	94	100	—

TABLE 9
Effect of Quantity of Zinc Upon the Benzene Bromination Rate

Quantity of Zn (in g.at.wts. per mole of Br_2)	Amount of reacted bromine (in %) for duration of experiment													
	30 min.	2 hrs.	6 hrs.	18 hrs.	27 hrs.	2 days	4 days	5 days	6 days	7 days	8 days	11 days	12 days	14 days
0.0025	2.6	3.8	6.3	9.7	13.4	19.3	27.2	31.4	33.9	36.4	39.4	44.8	46.9	—
0.005	2.1	4.7	10.5	20.6	28	43.1	65.3	74.9	78.2	85	89.2	95.6	100	—
0.01	3.8	8.0	15.1	28	34.3	46.9	67.8	71.8	76.6	82.5	87.0	95.9	100	—
0.02	2.6	8.0	15.9	28	33.9	44.4	59.2	67	72.4	77.4	84.6	93.3	97.7	—
0.04	6.7	12.2	19.3	30	34.8	44.4	52.3	56.5	59.9	61	67.8	78.7	83.3	—
0.1	2.5	3.8	5.5	12.2	18.9	31	56.5	67.4	72.3	79.1	85	93.3	97.7	100

TABLE 10
Bromination Products of Benzene

Reaction products	Yield of bromination products (in %) with catalyst							
	Without catalyst	Zn	Hg	Bi	Te	H_2O	HBr	CH_3COOH
	22 mo.	25 days	3 mo.	3 mo.	4 mo.	30 mo.	18 mo.	28 mo.
C_6H_5Br	20	100	100	100	100	6	100	10
$C_6H_6Br_6$	80	0	0	0	0	94	Traces	90

TABLE 11
Bromination Products of Toluene

Reaction products	Yield of reaction products (in %) with catalyst								
	Without catalyst	Cu	Mg	Zn	Cd	Hg	Al	Sn	Pb
$BrC_6H_4CH_3$	44	85	43	97	95	56.2	67	86	56.4
$C_6H_5CH_2Br$	56	15	57	3	5	43.8	33	14	43.6

Reaction products	Yield of reaction products (in %) with catalyst								
	Sb	Bi	Te	I	Fe	H_2O	HBr	C_6H_5I	$C_6H_4(NO_2)_2$
$BrC_6H_4CH_3$	84	95.4	95.8	93.4	95.9	Traces	49	54.4	25
$C_6H_5CH_2Br$	16	4.6	4.2	6.6	4.1	100	51	45.6	75

SUMMARY

1. Of the numerous catalysts used in bromination of aromatic compounds, the best have been found to be iron, zinc birmuth, mercury, cadmium and tellurium. During the reaction process, they are all converted into the corresponding bromides.

2. Zinc in the form of zinc dust can be recommended as a good, practical catalyst for bromination of benzene.

3. The evolution of hydrogen bromide in bromination accelerates further the course of the substitution reaction.

4. Water, acetic acid and aromatic nitro compounds decelerate, or have hardly any accelerating action on the substitution reaction. These compounds, water in particular, also effec the direction of the reaction in such manner that in the bromination of benzene, the content of hexabromocyclohexane is increased, and upon brominating toluene, more benzyl bromide is formed.

5. Upon bromination, catalysis can be homogeneous ($FeBr_3$, $AlBr_3$, HBr) or heterogeneous ($ZnBr_2$).

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INVESTIGATION OF ALLENE HYDROCARBONS

III. OXIDATION OF ALLENE HYDROCARBONS BY ACETYL HYDROGEN PEROXIDE

V. I. Pansevich-Kolyada and Z. B. Idelchik

The Prilezhaev reaction [1] has been studied in a large number of ethylene series hydrocarbons and their derivatives, but its applicability to the most highly unsaturated hydrocarbons has been given little study.

Prilezhaev studied the oxidation of phenylacetylene by benzoyl hydrogen peroxide [2]. Although the reaction took four months, the oxidation products gave him nothing on which to judge its chemistry. Prilezhaev [3] and Nametkin and Bryusov [4] oxidized the diolefin hydrocarbons, and obtained the mono- and dioxides depending upon the quantity of hydrogen peroxide. Muskat and Herman [5] oxidized cis-1-phenylbutadiene-1,3 with benzoyl hydrogen peroxide in chloroform at 0 and 25°. In the first instance they obtained 1-phenyl-3-benzoyl-oxybuten-1-ol-4 and in the second 1-phenyl-1,3-dibenzoyloxybutanediol-2,4. They isolated small quantities of the monoxide with oxide ring in the 3,4 position, and the dioxide, at the same time as they obtained the benzoyl derivatives.

Pummerer and Reindel [6] oxidized the same hydrogen peroxide in chloroethane at 0° with butadiene-1,3 and 2-methylbutadiene-1,3 and got only the monoxide, the second double bond not being affected in their opinion. With 2-methylbutadiene-1,3 the oxide ring was formed in the 1,2 position. Everett and Kon[7] oxidized benzoyl hydrogen peroxide in chloroform with ice-cooled monoxides of butadiene-1,3, 2-methylbutadiene-1,3, hexadiene-2,4, 2,3-dimethylbutadiene-1,3 and 1-phenylbutadiene-1,3. The dioxides were produced in each case. With the two last hydrocarbons, however, the pure dioxides were not isolated. Malenok, Sologub and Kulkina [8] oxidized acetyl hydrogen peroxide with vinylacetylene hydrocarbons and established that oxidation pertained only to the double bond, while the triple bond was titrated out with bromine after the reaction. We [9] oxidized 80-90% acetyl hydrogen peroxide in ether at 25° with 2,4-dimethylhexadiene-2,4, 2,4-dimethyloctadiene-2,4 and 2,4,7-trimethyloctadiene-2,4. In all cases the reaction products were dioxides and monoacetate glycol oxides.

This small group of studies constitutes the whole of the investigation of organic hydrogen peroxide oxidation by diolefin, acetylene and butadiene hydrocarbons. The effect of this oxidizing agent upon allene hydrocarbons has not been studied at all.

The works cited above testify to the lack of uniformity in the relation of organic hydrogen peroxides to various types of bonds. Therefore, study of the oxidation reactions of allene hydrocarbon organic hydrogen peroxides, which are often found with acetylene and butadiene hydrocarbons because of their mutual isomeric conversions, presents undeniable interest as a possible means of analyzing such mixtures. It is also important to find a means of establishing the structure of these hydrocarbon isomers, as the reliable ozonization method of resolving this problem is quite difficult, while the oxidation of acetylene hydrocarbons and their allene isomers with a one per cent permanganate solution is inapplicable for this purpose, as shown by Favorsky and Bon [10], as it gives identical reaction products. Finally, it is of interest to clarify the possibility of producing allene hydrocarbon dioxides, which have not been studied at all. The literature contains but a single example[11], tetraphenylallene dioxide, obtained by oxidizing that hydrocarbon with chromium anhydride.

In the present study, we oxidized 2-methylhexadiene-2,3 (I), 2-methyloctadiene-2,3 (II) and 2-methyl-4-phenylpentadiene-2,3 (III) with acetyl hydrogen peroxide.

Oxidation of hydrocarbon (I) was with 69.8% acetyl hydrogen peroxide in anhydrous ether. The amount of hydrogen peroxide was based on calculation for oxidation of both double bonds. The reaction was energetic and heat-producing, and within an hour virtually all the hydrogen peroxide had been used. A substance with b.p. 83-85° / 2 mm, analysis of which corresponded to monoacetate glycol oxide (IV) was isolated from the oxidation products. Its structure probably is that of (IV).

$$(CH_3)_2C=C=CH-CH_2-CH_3 \rightarrow (CH_3)_2C-C-CHOH-CH_2-CH_3 \rightarrow (CH_3)_2C-C-CH-CH_2-CH_3$$

$$\underset{O\ OCOCH_3}{\underset{V}{\qquad}} \qquad \underset{OCOCH_3}{\underset{O}{\qquad}} OCOCH_3$$
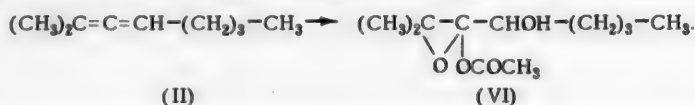
(I)   (IV)   (V)
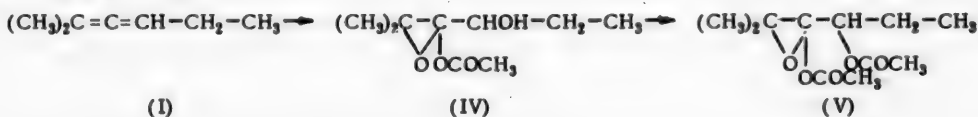
Compounds containing the oxide ring with an alcohol or ether group at the carbon atom of the ring, are known in the literature.
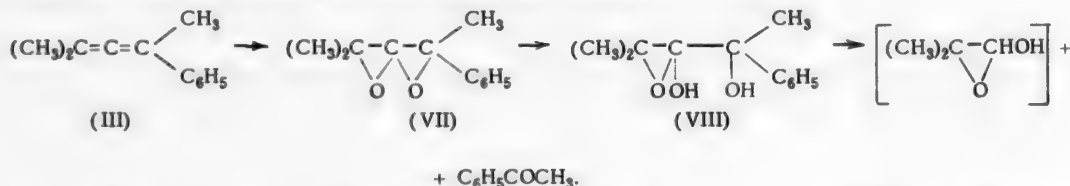
The first known substance of similar structure was Butlerov's oxoctenol [12], for which he proposed two equally probable formulas: a hydroxy acid and a keto alcohol.   Similar compounds were apparently obtained by Khaletsky [13] and Madelung and Oberwegner [14]. Favorsky [15], Danilov, Venus-Danilova and their pupils [16] accepted the formation of this hydroxy acid as the explanation for certain chemical processes. The work of Temnikova and associates [17] and also that of Stevens and associates [18] is entirely convincing proof of the possible existence of hydroxy acids of the given structure.

When monoacetate glycol oxide (IV) was reacted with acetic anhydride, the result was apparently the diacetate (V). In this reaction the oxide ring was not affected.

When hydrocarbon (II) was oxidized, the quantity of hydrogen peroxide used in the reaction corresponded to the two double bonds. The reaction products were exceedingly unstable and it did not prove possible to isolate them in pure form. However, the chemical character of the substance separated from the oxidation products and having b.p. 120-123° = 3 mm made it possible to regard it as being monoacetate glycol oxide (VI)

$$(CH_3)_2C=C=CH-(CH_2)_3-CH_3 \rightarrow (CH_3)_2C-C-CHOH-(CH_2)_3-CH_3.$$
$$\underset{O\ OCOCH_3}{\underbrace{\qquad\qquad}}$$

<div style="text-align:center">(II)   (VI)</div>

To obtain 2-methyl-4-phenylpentadiene-2,3 (III) we reacted phenyl magnesium bromide with mesityl oxide. The literature contains contradictory data on this reaction [19]. The 2-methyl-4-phenylpenten-2-ol-4   [20] of which we obtained a yield of up to 75% by this reaction was subjected to dehydration, giving 2-methyl-4-phenylpentadiene-2,3 (III). If the magnesia complex be decomposed by sulfuric acid, without cooling, one obtain no hydrocarbon (III) instead of alcohol. Oxidation of (III) with acetyl hydrogen peroxide wa' energetic and, as in the previous instances, was virtually complete within 30-40 minutes, while the consumption of hydrogen peroxide corresponded to the oxidation of two double bonds. The oxidation products included substance (VII) with b.p. 129 134°/2.5 mm, of which analysis gave reason to conclude that it was 2-methyl-4-phenyl-dioxido-2,3,3,4-pentane (VII).

$$(CH_3)_2C=C=C\overset{CH_3}{\underset{C_6H_5}{\diagdown}} \rightarrow (CH_3)_2C-C-C\overset{CH_3}{\underset{C_6H_5}{\diagdown}} \rightarrow (CH_3)_2C-C-C\overset{CH_3}{\underset{C_6H_5}{\diagdown}} \rightarrow \left[(CH_3)_2C-CHOH\right] +$$

<div style="text-align:center">(III)   (VII)   (VIII)</div>

<div style="text-align:center">+ C_6H_5COCH_3.</div>

Dioxide (VII) proved unstable, as Prilezhaev [21] had noted of the monoxide; each redistillation produced low-boiling fractions chiefly containing acetophenone and condensation products.

The production of acetophenone during distillation of the oxidation products of 2-methyl-4-phenylpentadiene-2,3 may be explained by the partial hydration of dioxide (VII), with production of glycol oxide (VIII); the latter, like certain pinacols [22], benzalacetone oxide [23], methylisobutenylphenylcarbinol oxide [19] and certain alcohol oxides [24], cleaves on distillation into acetophenone and more volatile products whose formation we failed to expect and therefore did not trap. It must be noted that 2-methyl-4-phenylpentadiene-2,3 (III) is oxidized by atmospheric oxygen upon long storage, and becomes a thick viscous mass. Attempts to distill these oxidation products resulted in violent decomposition, and again in the production of acetophenone.

The presence of acetophenone glycol oxide (VIII) in the decomposition products confirms the structure of hydrocarbon (III), oxidized by us, as 2-methyl-4-phenylpentadiene-2,3, and also indicates that the oxide ring to whose carbon atom the phenyl radical is attached is highly unstable.

Thus, the reaction of acetyl hydrogen peroxide with allene hydrocarbons of the aliphatic series results in oxidation of both double bonds, while the reaction products are monoacetyl derivatives of the glycol oxides (IV and VI). Monoacetyl derivative (IV) and acetic anhydride produce the diacetyl derivative of glycol oxide (V).

Oxidation of the phenyl-substituted allene hydrocarbon (III) also takes place at both double bonds. The reaction product is an extremely unstable dioxide (VII) which splits into acetophenone and more volatile products upon distillation.

As the oxidation of allene hydrocarbons took place very rapidly, and the acetylene bond of the organic hydrogen peroxides did not oxidize, this oxidizing agent may be used to characterize mixtures of allene and acetylene hydrocarbons or to determine the structure of these isomeric compounds.

1. Production of 2-Methylhexadiene-2,3.

Bromination of 2-methylhexanol-2 gave 2-methyl-2,3-dibromohexane.

B.p. 79-83° / 18 mm, n_D^{20} 1.4992, d_4^{20} 1.497 MR_D 50.51; calculated 50.05.

The dibromide was treated with twice   of caustic potash in 33% alcohol solution. The hydrogen bromide was separated by heating the mixture to boiling. After heating for two hours over a boiling water bath the reaction mixture was diluted with water, the precipitated monobromide was separated out, and driven off from the residue with water vapor. The alcohol was   with water, and the 2-methyl-3-b mohexene-2 was dried with calcium chloride and distilled. The yield attained 90% of theoretical.

B.p. 82-83° (70 mm), n_D^{20} 1.4700, d_4^{20} 1.1748, MR_D 42.03; calculated 41.95.

0.1912, 0.3301 g sub.; 22.94 g benzene: Δt 0.240, 0.425° Found: :M 178.7, 174. $C_7H_{13}Br$. Calculated: M 177.

The structure of the monobromide was demonstrated by permanganate oxidation. 8 g monobromide was emulsified in 100 ml water and 1000 ml of 1% $KMnO_4$ solution was added gradually as color was lost. After saturation with carbon dioxide and neutralization with potash, the residue was filtered, and the neutral volatile oxidation products were driven off the filtrate. The first 10-15 ml of distillate was processed with semicarbazide. The semicarbazone thus obtained melted at 123.5°. A sample mix of butyraldehyde with the semicarbazone did not result in lowering the melting point. The residue gave additional crystals of semicarbazone, which melted at 180-185°. A sample mixture of acetone with the semicarbazone melted at 181-185°. After the neutral volatile products were separated out, the distillate was acidified with sulfuric acid, and volatile acids were driven off. These products were treated with silver carbonate, and 3 fractions of silver salts were obtained, whose analysis showed the presence of butyric acid.

1st fraction 0.1830 g sub.: 0.1018 g Ag. 2nd fraction 0.1831 g sub.: 0.1018 g Ag. 3rd fraction 0.1496 g sub.: 0.0824 g Ag. Found %: Ag 55.62, 55.59, 55.14. $C_4H_7O_2Ag$. Calculated %: Ag 56.23.

2-Methylhexadiene-2,3 (I) was obtained by heating 100 g 2-methyl-3-bromo-hexene-2 and 200 g alcohol solution of caustic potash (66 g KOH and 134 g ethyl alcohol) in an autoclave for 7 hours at a temperature of 130-135°. The phosphorous bromide derived, which was always 50% of the theoretical, was filtered off; the hydrocarbon was distilled over a water bath to 80°, and the alcohol was washed with water. 520 g monobromide was treated in the same way. After washing with alcohol, the residue, amounting to 145 g, was dried with calcium chloride. Repeated distillation of the residue gave 30 g substance (12.6%).

B.p. 97-100° (748 mm) n_D^{20} 1.4351, d_4^{20} 0.7331, MR_D 34.2; calculated 33.59.

0.2179 g sub.: 0.6962 g CO_2; 0.2452 g H_2O. 0.1718. 0.3512 g sub.; 24.9 g benzene: Δt 0.344, 0.733°. Found %: C 87.13; H 12.59; M 103, 98.8. C_7H_{12}. Calculated %: C 87.50; H 12.50. M 96.

Oxidation of 2-methylhexadiene-2,3 with acetyl hydrogen peroxide

59 g 69.8% acetyl hydrogen peroxide, calculated for oxidation of both double bonds, was added gradually to 25 g hydrocarbon in 70 ml dry ether. The reaction was accompanied by much giving off of heat, so that the reaction mixture was cooled with snow water and the hydrogen peroxide was added slowly to prevent the temperature from rising above 25°. After 24 hours it was determined that 5.1 g unreacted hydrogen peroxide remained. Thereafter it was reduced in quantity very slowly, which could be attriubted to its decomposition. The acetic acid was neutralized by a 10% soda solution, and the ether layer was separated off, washed with water and dried with Na_2SO_4 with a small admixture of K_2CO_3.

Double distillation of the oxidation products isolated 7.6 g of a substance that boiled at 83-85° (2 mm). It dissolved in water and in various other solvents and was rapidly oxidized by permanganate.

n_D^{20} 1.4370, d_4^{20} 1.0181, MR_D 47.90; calculated 46.51.

0.1754, 0.1971 g sub.: 0.3743, 0.4232 g CO_2; 0.1421, 0.1623 g H_2O. 0.1288 g sub.: 16.26 ml CH_4(0°, 760 mm), 0.4383 g sub.: 3.9 ml 0.6 N KOH. 0.1545, 0.3129 g sub.; 25.8 g benzene: Δt 0.174, 0.350°. Found %: C 58.20, 58.55; H 9.00, 9.21; OH 9.64; CH_3COO 31.47. M 176.9, 178.1. $C_9H_{16}O_4$. Calculated %: C 57.50; H 8.50; OH 9.05; CH_3COO 31.38. M 188.

Condensation of monoacetate glycol oxide (IV) by acetic anhydride

3.7 g substance was heated 1.5 hours over a boiling water bath with 8.5 g acetic anhydride, and then boiled 4 to 5 hours. The mixture turned brown but became almost colorless upon cooling. 2.1 g substance of a thick consistency, which did not show active hydrogen, was isolated after double distillation.

B.p. 123.5-124° (7 mm), n_D^{20} 1.4325, d_4^{20} 1.0447, MR_D 57.16; calculated 55.88.

0.1774, 0.2086 g sub.: 0.3813, 0.4507 g CO_2 0.1298, 0.1536 g H_2O. 0.4191 g sub.: 39.2 ml 0.1 N NaOH after standing for 24 hours. 0.1508, 0.3359 g sub.; 16.35 g benzene: Δt 0.235, 0.507°. Found %: C 58.70, 58.93; H 8.33, 8.24; CH_3COO 54.6, M 201.7, 208.3. $C_{11}H_{18}O_5$. Calculated %: C 57.39, H 8.20; CH_2COO 51.3. M 230.

II. Production of 2-Methyloctadiene-2,3

Bromination of 2-methyloctanol-2 gave 2-methyl-2,3-dibromoctane.

B.p. 113-116° (13 mm), n_D^{20} 1.4902, d_4^{20} 1.3837, MR_D 59.57; calculated 59.47.

Treatment of the dibromide with alcoholic alkali gave the monobromide — 2-methyl-3-bromoketene-2.

B. p. 112-117° (56 mm), n_D^{20} 1.4660, d_4^{20} 1.0882, MR_D 52.17; calculated 51.23.

0.1734 g sub.: 0.1634 g AgBr. Found %: Br 40.10. $C_9H_{17}Br$. Calculated %: Br 39.03.

2-Methyloctadiene-2,3 was produced by heating 150 g 2-methyl-3-bromoctane-2 and 300 g of an alcohol solution of caustic soda (200 g alcohol and 100 g KOH) for 7 hours in an autoclave at 128-130°. The hydrocarbon was driven off at 112°, dried with calcium chloride and redistilled at 140-145° (744 mm). Yield was 9-10% of theoretical.

n_D^{20} 1.4370, d_4^{20} 0.7570, MR_D 42.90; calculated 41.88.

0.1670 g sub.: 0.5304 g CO_2; 0.1928 g H_2O. 0.1192 g sub: 20.77 g benzene: Δt 0.212°. Found %: C 86.62; H 12.92. M 132.8. C_9H_{16}. Calculated %: C 87.10. H 12.90. M 124.

The substance contained a small amount of displaced halide.

Oxidation of 2-methyloctadiene-2,3 by acetyl hydrogen peroxide.

24 g 81% acetyl hydrogen peroxide was added as it reacted to 22 g hydrocarbon in 44 ml ether at a temperature of not more than 25°. Oxidation was practically complete after 24 hours. The reaction products, treated as in the previous case, were double distilled in a vacuum. They proved to be unstable substances, and we were unsuccessful in isolating them in pure form, as partial decomposition occurred. 3.4 g of substance was separated, which boiled at 120-123° (3 mm), was readily discolored by permanganate and, when dissolved in organic solvents, revealed active hydrogen.

n_D^{20} 1.4415, d_4^{20} 0.9711, MR_D 58.80; calculated 55.75.

0.1955, 0.1468 g sub.: 0.4569, 0.3437 g CO_2; 0.1800, 0.1383 g H_2O. 0.1298 g sub.: 17.67 ml CH_4 (0°, 760 mm). 0.1260 g sub.: 17.4 ml CH_4 (0°, 760 mm). 0.0903, 0.1837 g sub.; 15.85 g benzene: Δt 0.157, 0.292°. Found %: C 63.60, 63.85; H 9.83, 9.83; OH 10.40, 10.34. M 186.8, 204. $C_{11}H_{20}O_4$. Calculated %: C 61.10; H 9.26; OH 7.87. M 216.

III. Production of 2-methyl-4-phenylpentadiene-2,3

600 ml 5% sulfuric acid was added to 150 g 2-methyl-4-phenylpenten-2-ol-4, produced as described previously [20]; the mixture was heated for two hours over a boiling water bath. 135 g of dehydration product was recovered and dried with calcium chloride. The result of triple vacuum distillation was a substance that boiled at 94-99° (9 mm), analysis of which coincided closely with that of 2-methyl-4-phenylpentadiene-2,3.

n_D^{20} 1.5537, d_4^{20} 0.9235, MR_D 54.83; calculated 53.08.

0.1954, 0.1959 g sub.: 0.6442, 0.6483 g CO_2; 0.1531, 0.1608 g H_2O. 0.1870, 0.3323 g sub.; 21.16 g benzene: Δt 0.300, 0.524°. Found %: C 90.35; H 8.77, 9.18. M 151.4, 154.1. $C_{12}H_{14}$. Calculated %: C 91.07; H 8.79, M 158.

Number of double bonds : 0.4533 g sub.: 0.9150 g Br. Found %: Br 66.88. $C_{12}H_{14}Br_4$. Calculated %: Br 66.92.

It must be noted that each redistillation of the hydrocarbon was accompanied by fractions boiling lower and higher, and that it proved impossible to obtain the hydrocarbon within narrower temperature limits.

Oxidation of 2-methyl-4-phenylpentadiene-2,3 by acetyl hydrogen peroxide.

87 g 69.8% acetyl hydrogen peroxide was poured slowly into 60 g hydrocarbon in 100 ml ether at not above 25°. Oxidation was very energetic. The mixture was left overnight in cold water. The next day 6.02 g acetyl hydrogen peroxide was found in the mixture, but only 0.54 g the day after that. The acetic acid was neutralized, first with a 10% soda solution, and then with dry soda. The ether extract was washed with water and dried with sodium sulfate. After the ether was driven off an oily liquid remained which when distilled even in high vacuum (2.5 mm), underwent considerable condensation and liberated acetophenone, which was the major component of the first fractions. Repeated redistillation produced 9.8 g of substance that boiled at 129-134° (2.5 mm). This was an oily yellow liquid,

readily oxidized by permanganate. It constituted a mixture with active hydrogen.

n_D^{20} 1.5210, d_4^{20} 1.0830, MR_D 53.32; calculated 53.16.

0.1932, 0.1878 g sub.: 0.5254, 0.5063 g CO_2; 0.1326, 0.1319 g H_2O. 0.1413 g sub.: 8.96 ml CH_4 (0°, 760 mm). 0.1339, 0.2833 g sub.: 25.8 g benzene: Δt 0.137, 0.287°. Found %: C 74.16, 73.61; H 7.68, 7.68; OH 4.84. M 194.7, 200.1. $C_{12}H_{14}O_2$. Calculated %: C 75.78; H 7.86. M 190. $C_{12}H_{16}O_3$. Calculated %: C 69.20; H 7.69; OH 16.3. M 208.

The substance of the first fractions smelled of acetophenone and distilled at 201.5° at normal pressure. Its semicarbazone had a m.p. of 197° after recrystallization. A sample mixed with acetophenone semicarbazone showed no reduction in melting ponit.

SUMMARY

1. Three allene hydrocarbons — 2-methylhexadiene-2,3 (I), 2-methyloctadiene-2,3 (II) and 2-methyl-4-phenyl-pentadiene-2,3 (III) were subjected to oxidation by acetyl hydrogen peroxide.

2. Oxidation of allene hydrocarbons by acetyl hydrogen peroxide takes place at both double bonds, with the formation of monoacetyl derivatives of the glycol oxides with hydrocarbons (I) and (II), and of an unstable dioxide in the case of hydrocarbon (III).

3. Oxidation with acetyl hydrogen peroxide may apparently serve as a means of analyzing mixtures of allenes with their acetylene hydrocarbon isomers.

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1)   See C. B. Translation, page a-151.
2)   "   "   "   "   page a-383.
3)   "   "   "   "   page 1197.
4)   "   "   "   "   page 1401.
5)   "   "   "   "   page 1567.
6)   "   "   "   "   page 1437.
7)   "   "   "   "   page a-197.
8)   "   "   "   "   page 231.

CONJUGATED ADDITION REACTIONS OF HALOGENS TO OLEFINS. I.

A. I. Titov and F. L. Maklyaev

The concept of conjugated reactions, developed by Shilov [1], has been assuming greater and greater significance.

By a conjugated reaction of halogens, the authors understand this to mean reactions in which a third component is involved in the interaction of halogens with olefins, wherein, however, the third component does not react by itself with the multiple bond under such conditions.

As an example of such reaction can be given the side formation of β-bromoethyl nitrate during the interaction of ethylene with bromine in potassium nitrate [2],

$$Br_2 + CH_2=CH_2 + KNO_3 \longrightarrow BrCH_2-CH_2-ONO_2 + KBr, \tag{1}$$

or the synthesis of chlorohydrins when passing olefins and chlorine into water [3,4], the synthesis of halogenated esters [5-18], the original chlorex method of Arbuzov [19],

$$Cl_2 + CH_2=CH_2 + CH_2-CH_2 \longrightarrow CH_2Cl-CH_2-O-CH_2-CH_2Cl \tag{2}$$
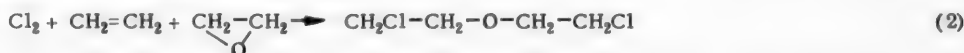
or the appearance of halogenated β-lactones by reaction of bromine with dimethylfumaric and with maleic acids [20].

In the authors' opinion, a majority of the addition reactions of halogens and of halogenating agents, of both ionic and radical character, to olefins can, under suitable conditions, become conjugated. In this series of works, however, the authors have considered only reactions of the ionic type.

To explain the involvement of a third component in the reaction of halogens with olefins, Gomberg [4], Ushakov [9], Conant [13], and Birckenbach [16] postulate that the first stage is an interaction of halogen with the third component, and the second — addition of this intermediate product to the olefin, for example:

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl, HOCl + CH_2=CH_2 \longrightarrow HOCH_2-CH_2Cl. \tag{3}$$
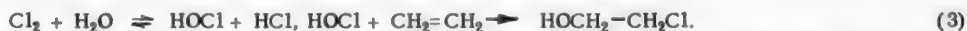
Shilov presented [22] convincing kinetic proofs of the inaccuracy of the above-postulated scheme. Such point of view is not at all applicable to an explanation of the involvement of sulfuric acid in the reaction (see further on), which was discovered by the authors, because in such a case the following unlikely reaction would need to be adopted:

$$Cl_2 + H_2SO_4 \longrightarrow ClOSO_3H + HCl. \tag{4}$$
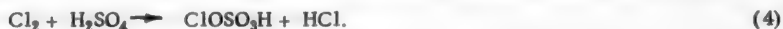
In addition, such reaction does not explain the formation of a trans-addition product.

Francis [2], Ingold, and others, postulate that the initial reaction phase consists of carbonium-ion formation:

$$Br \longleftarrow Br + CH_2=CH_2 \longrightarrow Br^- + BrCH_2-\overset{+}{C}H_2 \overset{Cl^-}{\longrightarrow} BrCH_2-CH_2Cl, \tag{5}$$
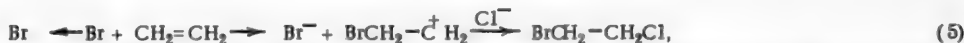
which reacts further with other particles, for example the chloride ion, according to Equation (5). Interaction of the same carbonium-ion in the second stage with bromide ion leads to formation of the usual reaction product — 1,2-dibromoethane. Objection to the appearance of a carbonium-ion in the case of purely aliphatic olefins should be made on the basis of energy principles [24]. The Ingold hypothesis is also negated by formation of various stereoisomeric halogen addition products to cis- and trans- isomers, because, according to such a concept, the latter would be obliged to produce as an intermediate one and the same cation, and hence, one and the same mixture of products. To make the Ingold interpretation agree with stereochemical data, Tarbell and Bartlett [25] consider that the second reaction phase proceeds very rapidly, and that the cations produced do not have time to assume one and the same planar configuration. With this thought in mind, Roberts and Kimball [26] postulate that the intermediate cation formed possesses an onium three-membered structure

$$Br-Br + C_6H_5CH=CHC_6H_5 \longrightarrow Br^- + C_6H_5CH-CHC_6H_5. \tag{6}$$
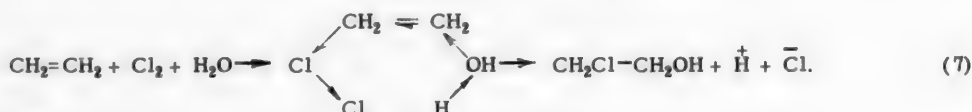$$\underset{Br^+}{}$$
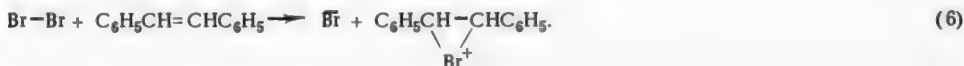
Thanks to cyclization variance in configuration is preserved, and the subsequent interaction, for example with bromide ion, accompanied by Walden inversion, leads to various trans-addition products. The viewpoint of Dewar [39]
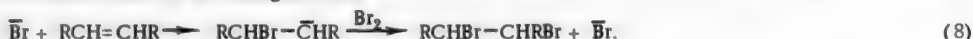
coincides with this hypothesis.

The Tarbell and Bartlett proposal does not eliminate the energy contradictions for reaction with purely aliphatic olefins, particularly for ethylene itself. In cases of halogen additions to cis- and trans-stilbenes, where the cation could have been sufficiently stable, formation of different products was nonetheless observed. The Roberts and Kimball hypothesis, despite instability of a three-membered ring, might apparently have been considered probable for iodine, and partially so for the bromine addition, but the formation of such onium compounds with chlorine or fluorine is improbable.

Shilov [21,22], with his coworkers, in extensive investigations of the kinetics of formation of ethylene chlorohydrin used the following scheme for presentation of the reaction mechanism, indicating by arrows the direction of migration of electrons:

$$\text{CH}_2=\text{CH}_2 + \text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{Cl} \underset{\text{Cl}}{\overset{\text{CH}_2 \;=\; \text{CH}_2}{\diagup}} \; \underset{\text{H}}{\overset{\text{OH}}{\diagdown}} \longrightarrow \text{CH}_2\text{Cl}-\text{CH}_2\text{OH} + \overset{+}{\text{H}} + \overset{-}{\text{Cl}}. \tag{7}$$

Similar schemes are to be found in the works of Hennion [17], Irwin [27], and other authors.

To explain variation in reaction products for cis- and trans-olefins, Ogg [28,29,30] advanced a hypothesis of primary addition along the double bond of the halogen anion

$$\overline{\text{Br}} + \text{RCH}=\text{CHR} \longrightarrow \text{RCHBr}-\overline{\text{CHR}} \xrightarrow{\text{Br}_2} \text{RCHBr}-\text{CHRBr} + \overline{\text{Br}}. \tag{8}$$

Acceptance of anion addition to nucleophilic olefins contradicts all chemical experience, however.

In 1946, the authors approached an understanding of the nature of conjugated addition reactions, and found new fields for application on the basis of the following concepts of the chemical nature of olefins and halogens.

Olefins are clearly defined, and effectively nucleophilic. This tendency, for example, is exemplified by their ability to give immediate coloration with tetranitromethane, as well as with standard bases, and to dissolve hydrogen fluoride and sulfur dioxide, apparently with formation of salt-like solvates. They enter into complex formation with numerous metallic halides of the aluminum chloride type, hydrogen bromide [31], and the like. In some olefins the basic properties are displayed so strongly that they are able to displace aniline from its hydrochloride, and even ammonia from ammonium chloride [32].

It has been considered that the carriers of the basic (electron donating) olefins are to be found in the π-bond. As is known, electrons of the π-bond are asymmetrically distributed with reference to the common axis of the carbon atoms (in other words, the G-bond), because of which they are mobile and sterically accessible to the action of electrophilic centers of other particles. These peculiarities of the π-bond we shall express by formulas of the type $\text{R}_2\text{C}\overset{\frown}{-}\text{CR}_2$, in which the π-electrons are designated by the arc; to simplify the outline, the usual schemes $\text{R}_2\text{C}=\text{CR}_2$ can be used, keeping in mind, however, their original context. From the above-stated point of view, complex formation of olefins, for example with Ag^+, can be expressed by the following equation, wherein the embedding of π-electrons into the cation sphere is indicated by the symbol $-->$

$$\text{Ag}^+ + \left(\underset{\text{CR}_2}{\overset{\text{CR}_2}{|}}\right) \longrightarrow \text{Ag}^+ \longleftarrow \left(\underset{\text{R}_2\text{C}^{+\delta}}{\overset{\text{R}_2\text{C}^{+\delta}}{}}\right). \tag{9}$$
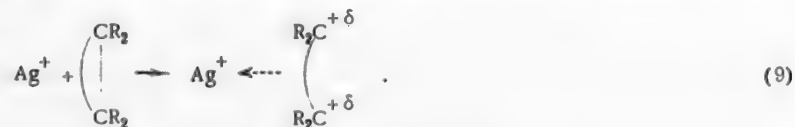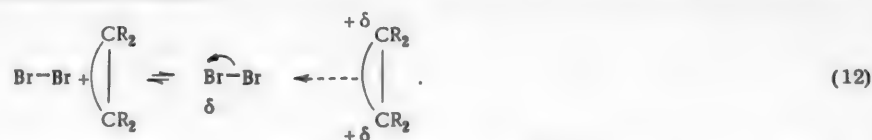
Such understanding of this process is confirmed by the decrease in combination frequencies of double bonds in the complex, due to deformation of the π-electron orbit.

In their chemical behavior, halogens display an active electrophilic behavior; they can, with adequate justification, be related to the aprotonic acids as interpreted by Lewis [33,34] and Usanovich [35]. The effective acidity of the halogens is evident from their ability to react rapidly with alkalies, amines, thioesters and many anions,

$$\text{R}_3\text{N} + \text{Br}-\text{Br} \rightleftharpoons \text{R}_3\text{N} \; \cdots\cdots \blacktriangleright \; \text{Br}\overset{\frown}{-}\text{Br}, \tag{10}$$

$$\overline{\text{Br}} + \text{Br}-\text{Br} \rightleftharpoons \overline{\text{Br}} \; \cdots\cdots \blacktriangleright \; \text{Br}\overset{\frown}{-}\text{Br}. \tag{11}$$

The arrow is this formula indicates displacement of the electronic density toward the halogen molecule, and the attendant possibility for strengthening the halide ion — up to the point of rupture — as happens to some degree in complexes with amines and amides.

Comparison of such data on the chemical nature of olefins and halogens leads to the conclusion that interaction between them is perhaps of an acid-base character
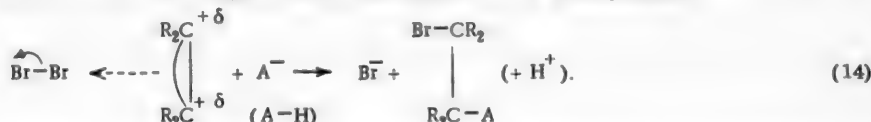
$$
Br-Br + \left(\!\!\begin{array}{c} CR_2 \\ \| \\ CR_2 \end{array}\!\!\right) \rightleftharpoons \quad \overset{\frown}{Br}-Br \quad \overset{\delta}{} \quad \longleftarrow\!\!-\!\!-\!\!-\!\!- \left(\!\!\begin{array}{c} \overset{+\delta}{CR_2} \\ \| \\ \underset{+\delta}{CR_2} \end{array}\!\!\right). \tag{12}
$$

This conclusion is strengthened by formation of molecular compounds of bromine with tetraarylethylenes [36]. The complexes are stable only upon cooling, and are dissociated at normal temperature. The complex formation and dissociation processes do not change the configurations of cis- and trans- isomers, in agreement with preservation of the double bond in the complex as adopted by the authors.

The most spectacular proof of existence of an acid-base interaction of halogens with olefins is the appearance of a brownish color, and a dipole moment (1.5 D) for the iodine in a solution of diisobutylene [37], which can be explained by formation of the complex:

$$
I-I + \left(\!\!\begin{array}{c} CR_2 \\ \| \\ CR_2 \end{array}\!\!\right) \rightleftharpoons \quad \underset{-2\delta}{I-I} \quad \longleftarrow\!\!-\!\!-\!\!-\!\!- \left(\!\!\begin{array}{c} \overset{+\delta}{CR_2} \\ \| \\ \underset{+\delta}{CR_2} \end{array}\!\!\right). \tag{13}
$$

With iodine solution in saturated hydrocarbons, no increased polarization was found, nor was a dipole moment therefor found. In this sense, iodine behaves similarly to some other aprotonic acids. We might mention that iodine catalyzes many reactions which are accelerated by acids.

Carbon atoms of the complex (Equation 12) should be highly electrophilic, with steric accessibility for interaction from the side opposite to the halogen molecule. This permits, in accordance with the general theory of alkylating agents [40], one to consider ready interaction of the complex (Equation 12) with anions, A^-, or their donors ($A-H$), with the formation of addition products of olefin and halogen atom and grouping A in the trans-position:

$$
\overset{\frown}{Br}-Br \quad \longleftarrow\!\!-\!\!-\!\!-\!\!- \left(\!\!\begin{array}{c} \overset{+\delta}{R_2C} \\ \| \\ \underset{+\delta}{R_2C} \end{array}\!\!\right) + A^- \longrightarrow \quad Br^- + \left(\!\!\begin{array}{c} Br-CR_2 \\ | \\ R_2C-A \end{array}\!\!\right) \ (+ H^+). \tag{14}
$$

A combination of Equations (12) and (14) represents, in the authors' opinion, the mechanism of conjugated addition reactions of halogen with involvement of the third component — the anion, or its donor.

If A^- be considered the halogen anion, or $H-A$ a molecule of hydrogen halide, then a combination of Equations (12) and (14) will express the addition mechanism of the halogens themselves in accordance with the ionic complex type. In conformity with this fact, Shilov [21] demonstrated that side reaction formation of dichloroethane during synthesis of ethylenechlorohydrin proceeds in proportion to the concentration of chloride ion; an analogous effect of concentration of halide ion and hydrogen halide has been observed in coupling reactions of the same type. An increase in the reaction rate of bromine with ethylene by 50-130-fold with decrease of temperature from 25 to 0° [38] is found to be in accordance with the assumption of complex formation role; the accelerating action of small amounts of added water upon this reaction, and the effect of polarity of the reactor walls, also confirm this hypothesis.

By schemes analogous to (14), the course of more complex conjugated reactions of halogens with olefins can be presented. For example, synthesis of chlorex according to Equation (2) occurs, in the authors' opinion, through the appearance of an onium complex:

$$
\overset{\frown}{Cl}-Cl \ \longleftarrow\!\!-\!\!-\!\!- \left(\!\!\begin{array}{c} \overset{+\delta}{CH_2} \\ | \\ \underset{+\delta}{CH_2} \end{array}\!\!\right) + O\!\!\left(\!\!\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array}\!\!\right) \longrightarrow Cl^- \left[\begin{array}{c} ClCH_2 \\ | \\ CH_2-\overset{+}{O}\!\!\left(\!\!\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array}\!\!\right) \end{array}\right] \begin{array}{l} \nearrow \begin{array}{c} ClCH_2 \\ | \\ ClCH_2 \end{array} + O\!\!\left(\!\!\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array}\!\!\right) \ (a) \\[2em] \searrow \begin{array}{c} ClCH_2 \quad CH_2Cl \\ | \qquad | \\ CH_2-O-CH_2 \end{array} \ (b) \end{array} \tag{15}
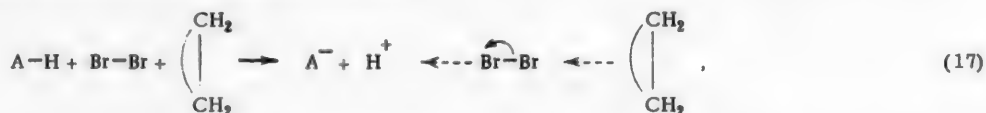$$
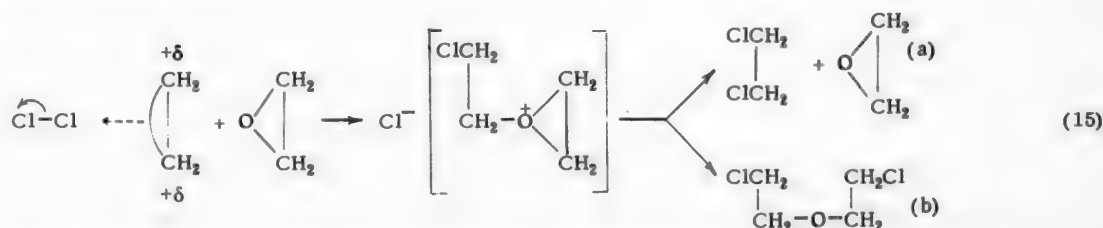
Alkylation of chloride ion with onium complex leads to formation of dichloroethane (a) or to chlorex (b).

The authors have demonstrated for the first time that a mixture of halogen and olefin is able, under appropriate conditions, not only to alkylate electrodonating molecules and salts, but also very strong, free acids,*themselves, sulfuric, benzene, and chlorosulfonic, which cannot be done by the usual and even most vigorous alkylating means. This makes it possible to consider halogen with olefin complex to be the strongest β-halogenalkylating agent available.
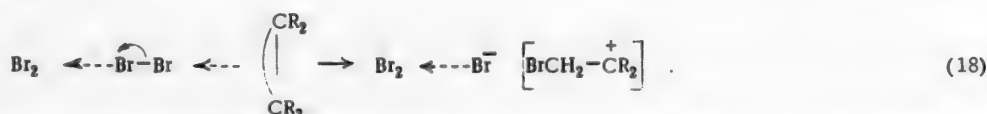
$$\overset{\frown}{Cl-Cl} \;\blacktriangleleft\!\text{-}\!\text{-}\!\text{-}\; \left(\!\!\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}\right. + H_2SO_4 \longrightarrow \bar{Cl} + \begin{array}{c} Cl-CH_2 \\ | \\ CH_2-O-SO_3H \end{array} + \overset{+}{H}\,. \tag{16}$$
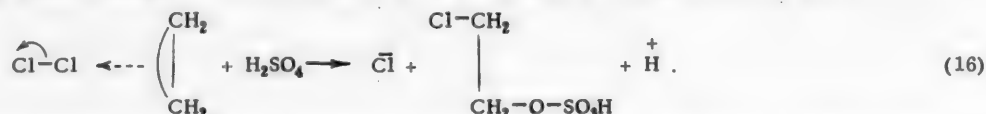
By the method of conjugated reaction – by simultaneous introduction of halogen and olefin to anhydrous acids – it was possible to achieve in good yields the synthesis of β-haloalkyl esters of many different acids.

It is quite possible that in these reactions the strong acids, A – H, promote formation of a complex of type (12) by means of increased polarization of the halogen molecule,

$$A-H + Br-Br + \left(\!\!\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}\right. \longrightarrow A^- + H^+ \;\blacktriangleleft\!\text{-}\!\text{-}\!\text{-}\; \overset{\frown}{Br-Br} \;\blacktriangleleft\!\text{-}\!\text{-}\!\text{-}\; \left(\!\!\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}\right. , \tag{17}$$

which is confirmed by the authors' observations concerning acceleration of halogenation of benzene with bromine water upon addition of sulfuric acid. Aprotonic acids of aluminum chloride, and especially the silver and mercury cations, can play an analogous role in activation of halogen. Halogen excess should also act in similar manner, which at times may lead to the appearance of salt-like perhalides [41] under conditions favorable for coupling of the cationoid carbon atoms with R radicals.

$$Br_2 \;\blacktriangleleft\!\text{-}\!\text{-}\!\text{-}\; \overset{\frown}{Br-Br} \;\blacktriangleleft\!\text{-}\!\text{-}\; \left(\!\!\begin{array}{c} CR_2 \\ \| \\ CR_2 \end{array}\right. \longrightarrow Br_2 \;\blacktriangleleft\!\text{-}\!\text{-}\!\text{-}\; Br^- \left[BrCH_2-\overset{+}{C}R_2\right]\,. \tag{18}$$

The formation of substitution products during interaction of olefins with halogens takes place, in the authors' opinion, because of the display of a σ, π-conjugation effect in the complex

$$Cl-Cl \;\blacktriangleleft\!\text{-}\!\text{-}\!\text{-}\; \left(\!\!\begin{array}{c} CR-H \\ \\ CR_2 \end{array}\right. \longrightarrow \bar{Cl} + \left(\!\!\begin{array}{c} ClCR \\ \| \\ CR_2 \end{array}\right. + H^+ \tag{19}$$
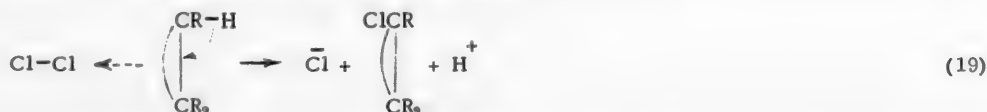
Substitution becomes unusual in the case of considerable stabilization of the π-bond, as for example, with aromatic rings.

It is expedient to examine a great number of other reactions of unsaturated compounds with electrophilic reagents from the point of view developed above. As the simplest example of processes of the type the formation of methoxyethylmercury acetate by interaction of ethylene with mercury acetate in methanol [42], bringing the latter into reaction

$$(CH_3COO)_2Hg \;\rightleftharpoons\; 2CH_3COO^- + Hg^{++}$$

$$CH_3COO^- + Hg^{++} + \left(\!\!\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}\right. \;\rightleftharpoons\;$$

$$CH_3COO^-Hg^{++} \;\blacktriangleleft\!\text{-}\!\text{-}\!\text{-}\; \left(\!\!\begin{array}{c} {}^{+\delta}CH_2 \\ \| \\ {}_{+\delta}CH_2 \end{array}\right. \overset{CH_3OH}{\longrightarrow} \tag{20}$$

$$\longrightarrow CH_3COOHgCH_2-CH_2OCH_3 + H^+,$$

---
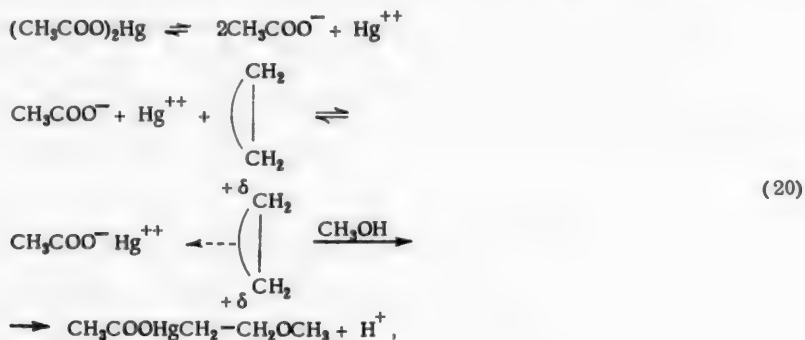
* See article II[J. Gen. Chem. 24, 1631 (1954)](C. B. Translation page 1613)

is similar to the interaction of halogens with olefins in alcoholic medium. In this respect Nesmeyanov [43] and coworkers demonstrated that addition of mercuric chloride to acetylene under the usual conditions proceeds in the trans-position.

$$Cl^- + Cl-Hg^+ + \overset{CH}{\underset{CH}{|||}} \rightleftharpoons Cl-Hg \longleftarrow \cdots \overset{CH}{\underset{CH}{|||}} + Cl^- \longrightarrow \overset{CHCl}{\underset{ClHgCH}{\Big(}} \qquad (21)$$
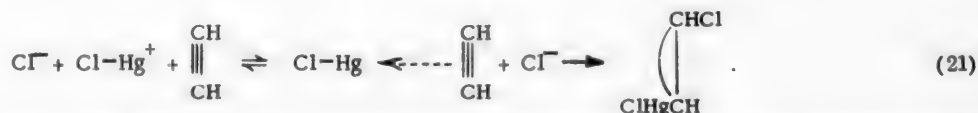
In the gaseous phase, when interaction cannot go according to the conjugated type of reaction, there results cis-isomers [44], i.e., direct addition actually occurs

$$Cl-\overset{Cl}{\overset{|}{Hg}}{}^{+\delta} + \overset{CH}{\underset{CH}{|||}} \rightleftharpoons \overset{Cl}{\underset{Cl-Hg}{|}} \overset{\cdots\rightarrow CH}{\underset{\longleftarrow\cdots CH}{|||}} \longrightarrow \overset{ClCH}{\underset{ClHgCH}{\Big(}} \qquad (22)$$
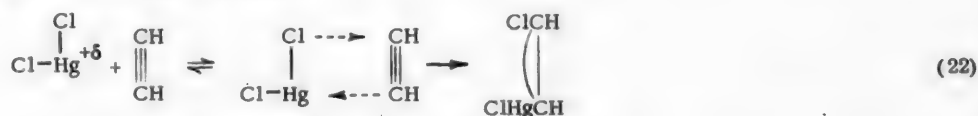
Evidently, addition in the cis-position, though hindered somewhat, is not excluded as a type of interaction with halogens.

Addition along multiple bonds of electrophilic compounds in the presence of bases no doubt also proceeds according to a conjugated type of reaction, for example in the case of hydroxylamine addition to mesityl oxide, or the addition of alcohol to tetrafluoroethylene in the presence of alcoholate [45].

$$\overset{F}{\underset{F}{>}}\underset{+\delta}{C}-\underset{+\delta}{C}\overset{F}{\underset{F}{<}} \xrightarrow{\bar{O}C_2H_5} \overset{F}{\underset{F}{>}}\underset{\delta}{C}-C\overset{F}{\underset{F}{<}} \longleftarrow \cdots \bar{O}C_2H_5 \xrightarrow[-\bar{O}C_2H_5]{HOC_2H_5} H-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-OC_2H_5. \qquad (23)$$
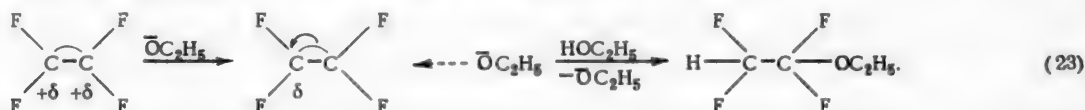
The difference consists in the fact that because of electron attraction of the negative substituents (CO, F, etc), the unsaturated compounds become the acceptor of electrons of the second component (H_2NOH, $C_2H_5O^-$), and the third component plays the role of donor of protons (C_2H_5OH).

SUMMARY

1. The concept of conjugated reactions for halogen addition along multiple bonds has been introduced, and a review presented.

2. It has been demonstrated that halogen molecules display properties of a strong aprotonic acid (effective electrophilia), and olefins in somewhat less effective manner, possess a basic character due to the relatively weakly-bound π-electrons.

3. It has been accepted that the initial phase of halogen reaction with olefins is the reverse of complex formation of acid-base nature (Equation 12).

Carbon atoms in such a complex possess high effective electrophilic character, and steric accessibility in the trans-position to halogen, thanks to which fact the complex can serve as a most potent β-halogenalkylating material, able to alkylate even the strongest acids (Equation 14).

4. From the point of view developed, the general mechanism, and special cases of halogen interaction with unsaturated compounds according to an ionic mechanism, have been defined.

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CONJUGATED ADDITION REACTIONS OF HALOGENS TO OLEFINS

II. SYNTHESIS OF β-HALOETHYLESTERS OF BENZENE- AND p-TOLUENESULFONIC ACIDS AND OF β-CHLOROETHYL SULFATES, CHLOROSULFONATE, PHOSPHATE AND MIXED 1,2-DIHALOETHANES

A. I. Titov and F. L. Maklyaev

According to the first article [1] the conjugated reaction of halogens with ethylene begins with formation of a complex, whose structure can be represented by the formula

$$
\widehat{Br-Br} \;\blacktriangleleft\!----\; \left(\!\!\begin{array}{c} +\delta \\ CH_2 \\ | \\ CH_2 \\ +\delta \end{array}\right. , \tag{1}
$$

in which the dotted arrow indicates embedding of the π-electrons into the electrophilic halogen atom.

Thanks to steric accessibility of the electrophilic carbons in trans-position relative to bromine, the complex is very readily alkylated, being the donor of the β-bromoethyl cation. This allows wide application of the simultaneous action of halogen and olefin for introducing β-haloalkyl groups into various molecules.

The main purpose of the present work was to find synthetic methods for preparing β-haloethyl esters of sulfonic acids according to the method of conjugated reaction, by directing the alkylating action of the complex upon a third component present. For this purpose, the action of ethylene and bromine upon benzenesulfonic acid salt solution was first tried out

$$
Br_2 + CH_2=CH_2 + C_6H_5SO_3^- \longrightarrow Br^- + C_6H_5SO_2OCH_2CH_2Br. \tag{2}
$$

The yield of ester, of course, increased with increasing concentration of salt, but even in a saturated solution of potassium benzenesulfonate it only slightly exceeded 10%.

In addition, the authors were able successfully to, replace the salts by the free acids. The sulfonic acids water and hydrogen bromide liberated during the course ot reaction were subject to the acylating action of the complex, leading, respectively to the production of ethylenebromohydrin, dibromoethane, and β-bromoethylsulfonate. The relationships observed can be illustrated by the data of one experiment on a conjugated reaction course in p-toluenesulfonic acid solution, combined in Scheme (3).

$$
\widehat{Br-Br} \;\blacktriangleleft\!----\; \left(\!\!\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array}\right.
\begin{array}{l}
\xrightarrow{\;62\%\ ArSO_3H\;} ArSO_2OCH_2CH_2Br\ (\text{yield }19\%) \\
\xrightarrow{\;35\%\ H_2O\;} HOCH_2CH_2Br\ (\text{yield }34\%) \\
\xrightarrow{\;\sim 3\%\ HBr\;} BrCH_2CH_2Br\ (\text{yield }47\%)
\end{array} \tag{3}
$$
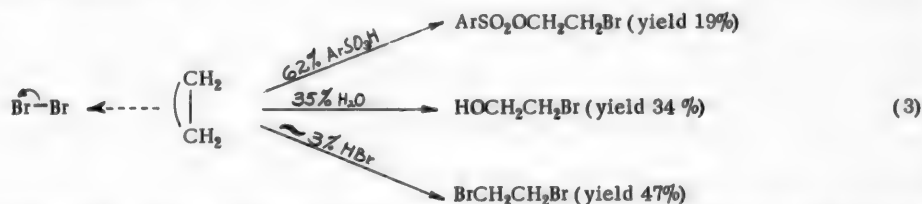
The ratio of reaction product yield to molar concentration of corresponding alkylate component can be called the activity coefficient for this reaction. If the activity coefficient for water (f_{H_2O}) is taken to be unity, then for the above-indicated case

$$
f_{H_2O} : f_{ArSO_3H} : f_{HBr} \sim 1 : 3.2 : 700. \tag{4}
$$

One should conclude from the ratio (4) an extremely high activity for hydrogen bromide, or bromide ion, respectively, in the conjugated reactions. With low hydrogen bromide concentrations, and other conditions the same, yield of dibromoethane is increased in almost direct proportion to the analytical content of hydrogen bromide, and the yields of ester and of ethylene bromohydrin are respectively decreased, as can be seen from the experimental data with 64% p-toluenesulfonic acid solution (Table 2). The activity of hydrogen chloride, or of chloride ion, respectively was 10-15 times less, as from the authors experiments on synthesis of chlorobromoethane and of β-chloroethylbenzenesulfonate, according to the conjugated reaction method.

A comparison of all these results makes possible the deduction that for optimal course of conjugated reaction of ethylene with halogen in sulfonic acid solution in the direction of β-haloethylsulfonate formation, it is necessary: 1) to use anhydrous sulfonic acids as far as possible, 2) to use chlorine as the halogen, 3) to facilitate removal of hydrogen chloride. In fact, yield of β-chloroethylbenzenesulfonate was up to 80% upon interacting ethylene with chlorine in anhydrous benzenesulfonic acid melt at 60° under the condition of bathing the entire surface of the reactor with melt. It is possible that a portion of the dichloroethane formed during this time is due to intramolecular regrouping of the complex by reaction not in contact with the sulfonic acid melt, and possibly some other process, for example:

$$C_6H_5SO_3CH_2CH_2Cl + HCl \longrightarrow C_6H_5SO_3H + ClCH_2CH_2Cl.$$

The conjugated reaction of ethylene and chlorine in concentrated sulfuric acid makes possible a good yield of di-(β-chloroethyl)-sulfate (via the acid ester formation stage). Reaction in chlorosulfonic acid leads to formation of β-chloroethylchlorosulfonate, and in phosphoric acid, to tri-(β-chloroethyl)-phosphate.

Let us consider the question of activity of three components in the reactions described. No doubt the activity of the anions and of the salts is greater than of the corresponding acids, for example $f_{SO_4''} > f_{HSO_4'} > f_{H_2SO_4}$. As a first approximation, it can be looked upon as a proportional power of the basic properties of the particle, or, as an inverse proportional power of the acid properties, for example, $f_{NH_3} > f_{H_2O} > f_{CH_3COOH} > f_{CCl_3COOH}$ or $f_{OH'} > f_{CH_3COO'} > f_{CCl_3COO'}$.

A number of other factors, however — polarizability, dimerization, formation of stable solvates, steric factors, structural peculiarities — can, at times, change the indicated order of activities. Thus, the almost insignificant activity of fluoride ion, despite the considerable weakness of hydrofluoric acid in aqueous solution, should be related to the low polarizability of F^- as compared with other halide ions, and the stability of its hydrates, of the type $\overset{-\delta}{F} \cdots \to H-O-H$. The alkylating action upon such hydrates is apparently directed basically to the oxygen.

EXPERIMENTAL

1. Bromoethylation of Potassium Benzenesulfonate. A mixture of 500 g of 50% salt solution and 10.5 ml of bromine was saturated with ethylene with shaker agitation. The addition of bromine, and saturation with ethylene, was repeated. The oily reaction product was washed with water and dried with magnesium sulfate. There resulted the fractions: 25.9 g (33%) of dibromoethane, and 11.2 g (11%) of β-bromoethylbenzenesulfonate with b.p. 198-200° (15 mm).

2. Bromoethylation of Benzene- and p-Toluenesulfonic Acids in Aqueous Solutions. 400 g of a 60% solution of p-toluenesulfonic acid in mixture with 10.5 ml of bromine was saturated with ethylene with vigorous stirring. The addition of bromine, and the saturation with ethylene, were repeated. The reaction mixture was then diluted with 600 g of water the oily reaction product dried, and then fractionated. 35 g (46%) of dibromoethane and 24 g (21.5%) of β-bromoethyl-p-toluenesulfonate resulted.

B.p. 173-174° (2-3 mm), d_4^{20} 1.531, n_D^{20} 1.5472.
Found %: Br 28.4. $C_9H_{11}O_3SBr$. Calculated %: Br 28.6.

For analysis, according to Volhard, 0.5 g of the ester was boiled, first for 3 hours with 50 ml of water, and then for the same time with added 1 g of NaOH and immediate heating with the alkali, there was formed at once vinyl bromide.

TABLE 1

Experiment No.	Water (in g)	Yield (in %)	
		Ester	Dibromoethane
1	108	19	46
2	408	13	28
3	1608	6	14

TABLE 2

Experiment No.	Sulfonic acid solution (in g)	HBr (average)(in %)	Yield (in %)	
			Ester	Dibromoethane
1	600	1.8	29	33
2	400	2.2	22	45
3	200	3.2	14	63

With increasing amounts of water taken for reaction with 192 g of sulfonic acid, the amount of ethylene bromohydrin was increased, and the yields of ester and dibromoethane decreased (see Table 1).

Upon saturating the sulfonic acid solution of composition corresponding to Experiment 1 of Table 1 with 20 g

of hydrogen bromide, the yield of ester was decreased two-fold (9.1%), and the yield of dibromoethane increased to 64%. The effect of hydrogen bromide concentration can also be seen from the following series of experiments with varied amounts of 64% solution of p-toluenesulfonic acid (Table 2).

No noticeable variations in the reaction course were observed in light and in the dark. In experiments with gradual introduction of bromine, the yield of ester was increased somewhat. Upon carrying out the reaction in alcohol, side formation of ethyl-p-toluenesulfonate was observed, due to appearance of esterification.

3. Chloroethylation of Benzenesulfonic Acid. Reaction of ethylene with chlorine in a solution or melt of benzenesulfonic acid was carried out in a cylindrical glass reactor with round bottom. Tubes for chlorine, ethylene, and the outgoing gases were attached by ground-glass joints, as well as the stirrer with a liquid seal of β-chloroethylbenzene sulfonate. Gas feed from the gasometer was regulated by rheometers, the gasometer for chlorine being filled with sodium chloride or calcium chloride solution. The outgoing gases were metered into a trap with reflux condenser, washed with water, and collected in the gasometer. Heating was carried out on a water bath with automatic thermoregulator. Vigorous stirring ensured bathing of reactor top with the reaction mixture.

Pure benzenesulfonic acid was prepared as follows: the benzenesulfonyl chloride was heated for 1 hour under reflux with half the amount of alcohol, and the same volume of water then gradually added and heating continued on the water bath to disappearance of oily droplets of ester. Alcohol and water were distilled off at 20 mm up to 92% content of benzenesulfonic acid (m.p. 50-55°), and then at 2-3 mm at about 150°, 96-98% of product resulting.

456 g of melted 96% benzenesulfonic acid (2.75 moles) was charged into the reactor (700 ml capacity) and at a bath temperature of 60°, with vigorous stirring, 19.6 liters of chlorine (0.87 mole) passed through over a period of 2 hours, and 25 liters of ethylene (1.03 moles); about 8 liters of outgoing gases with 55% water content was collected. Increase in weight of reaction mixture was 61 g. It was diluted with magnesium sulfate, with added magnesium oxide to bind acid radicals. After distilling off the dichloroethane at 150-154° (4 mm), the β-chloroethylbenzene sulfonate was distilled off. Ester yield was 124.7 g (77% of theory based on total reaction products, or 65% according to chlorine) and dichloroethane was isolated in the amount of 16.3 g (23 and 19% respectively).

d_4^{20} 1.352, n_D^{20} 1.530 [2].
Found %: Cl 16.0. $C_8H_9O_3SCl$. Calculated %: Cl 16.1.

Upon passing 5 mole portions of chlorine and ethylene through, there resulted more than 500 g of the ester. When aqueous acid was used, the yield was decreased, but to a lesser extent than in experiments with bromine, due to the lower activity of chloride ion; thus, for a 60% solution, the ester yield was about 30%, dichloroethane 20%, and ethylene chlorohydrin 40%.

4. Chloroethylation of Sulfuric, Chlorosulfonic and Phosphoric Acids.

a) 224 g of sulfuric acid (d 1.84) was poured into the reactor (150 ml capacity) and under the conditions indicated earlier, it was saturated with ethylene and chlorine at a gas rate of 150 ml per minute.

Passage of gases was discontinued when a sample of the reaction mixture remained about $^9/_{10}$ insoluble upon mixing with an equal volume of water, and the relative content of sulfuric acid in it corresponded to about 5%, which necessitated passing through 100 liter portions of chlorine and ethylene. After the above-described treatment and fractionation, about 150 g of ester resulted:

B.p. 143° (3 mm), d_4^{20} 1.4838, n_D^{20} 1.463, corresponding to the literature data [3,4].

After 6 hours boiling of the ester with excess water, it was possible to titrate the theoretical amount of chloride ion according to the Volhard method.

b) 125 ml of chlorosulfonic acid was poured into the reaction mixture, and with ice cooling, over a period of 20 minutes, 4 liters of ethylene and 5 liters of chlorine passed through. Everything was then poured onto ice and extracted with ether. From the dried extract, a fraction, b.p. about 90° (16 mm), was isolated with properties described for β-chloroethylchlorosulfonate [5].

c) Reaction in Phosphoric Acid Carried Out at Normal Temperature. In order to obtain the ester intermediate, it was necessary to pass through a considerable excess of chlorine and ethylene. After treatment similar to that described above, there resulted trichlorotriethylphosphate:

B.p. 180-182° (3 mm), d_4^{20} 1.422, n_D^{20} 1.475 [6,7].

5. Bromoethylation of Sodium Chloride and Hydrogen Chloride. A mixture of 750 ml of 25% sodium chloride solution and 32 g of bromine was saturated in the shaker with ethylene. After washing and drying, the organic layer

was distilled in a dephlegmator. The following fractions were obtained: 1st – 108-112°, 9.4 g; 2nd – 112-116°, 5.0 g; 3rd – 126-130°, 1.8 g. These data made it possible to consider that the content of chlorobromoethane in the reaction product amounted to about 70-80%. Colorless crystals, m.p. 104-107°, resulted from the residue in the flask after extraction with ether and purification with charcoal, which was not investigated further.

Reaction in 150 ml of hydrochloric acid was carried out in a reactor of 200 ml capacity. Bromine was introduced through a dropping funnel with tube reaching to the bottom. With stirrer in operation, and an ethylene passage rate of 200 ml/minute, the addition of bromine at normal temperature was carried out in such manner that its color was not noticeable in the solution. After diluting the reaction mixture with water, and further standard treatment, the following fractions resulted: 1st – 106-112°, 23 g; 2nd – 112-126°, 9.6 g; 3rd – 126-134°, 8.4 g. The residue of 4.7 g was not investigated further. The content of chlorobromoethane in reaction product amounted to about 65%.

Attempt at synthesis of fluorobromoethane was unsuccessful. Interaction of bromine and ethylene in potassium fluoride solution led, on the whole, to formation of ethylene bromohydrin and in the case of hydrofluoric acid, to dibromoethane, while fluorobromoethane could be detected only qualitatively through reactions for the fluoride ion after heating the first distillate with sodium in toluene in a sealed tube at 100°.

SUMMARY

1. Under suitable conditions, a mixture of halogen and ethylene can serve as a vigorous means of β-haloethylation, which action in the solution is distributed over all suitable molecules and anions in proportion to the product of activity and concentration of each of these particles.

2. It has been found that better yields of β-bromo- and β-chloroethyl esters of benzene- and p-toluenesulfonic acids (up to 80%) can be attained when the conjugated reaction of chlorine and ethylene is carried out in melts of anhydrous sulfonic acids under conditions which promote removal of hydrogen chloride and dichloroethane, and keeping to a minimum the interaction on unbathed reactor walls.

3. According to the method of conjugated reaction synthesis di-(β-chloroethyl)-sulfate, β-chloroethylchlorosulfonate, tri-(β-chloroethyl)-phosphate, chlorobromoethane and fluorobromoethane formations have been qualitatively demonstrated.

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INVESTIGATION IN THE FIELD OF UNSATURATED CYCLIC HYDROCARBONS AND THEIR HALOGEN DERIVATIVES

XV. REACTION OF METALLIC SODIUM WITH 1,4-DIBROMOCYCLOHEXENE-2

N. A. Domnin and A. S. Beletskaya

In 1903, Zelinsky and Nametkin [1] observed that in the reaction of metallic sodium with a mixture of cis-trans-1,4-dibromocyclohexanes, there was formed dicyclo-(2,0,2)-hexane along with the mixture of products having the composition C_6H_{10}.

Later, Zelinsky and Kocheshkov [2] demonstrated that in the reaction of metallic sodium with trans-1,4-dibromocyclohexane in anhydrous amyl ether, there is formed the cyclohexadiene-1,3 and diallyl, and with cis-1,4-dibromocyclohexane, the dicyclo-(2,0,2)-hexane is formed.

Although it was not consistently and convincingly proved in either investigation that dicyclo-(2,0,2)-hexane can exist, nevertheless, it is of very great interest, inasmuch as it pertains to the solution of an important stereochemical problem, namely, the ability of a very strongly deformed, and the simplest of dicyclic systems, to exist.

In light of these investigation results, the authors considered it of interest to study these reactions which take place during interaction of metallic sodium with 1,4-dibromocyclohexene-2. It might be expected that interaction would go according to one of the following systems:

(I)

(II)
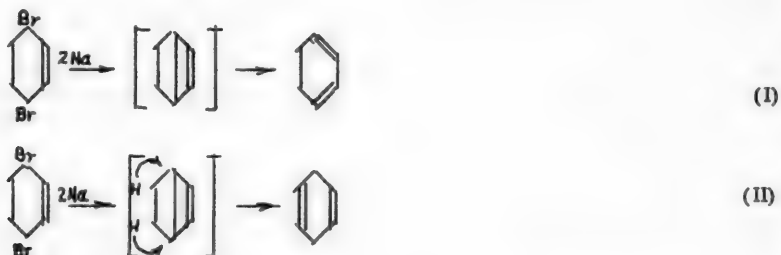
According to Scheme (I), in time, the dicyclo-(2,0,2)-hexene-2 appearing by rearrangement of the double and the bridge bonds, converts to the conjugated system, cyclohexadiene-1,3. According to Scheme (II), in time, the dicyclo-(2,0,2)-hexene-2 which appears through rearrangement of two hydrogen atoms from the methylene groups in positions 1,4, converts into the system with isolated double bonds — cyclohexadiene-1,4.

As the result of this work, the authors have demonstrated that interaction of metallic sodium with 1,4-dibromocyclohexene proceeds according to Scheme (I), as the result of which only cyclohexadiene-1,3 is formed.

Thus, the authors have demonstrated that with equal possibility of formation of a six-membered ring with isolated or conjugated bond systems, the latter forms preferentially to the former.

EXPERIMENTAL

Synthesis of cyclohexadiene-1,3. 40.3 g of 1,2-dibromocyclohexane was added to 50 g of freshly-distilled, boiling quinoline in a flask equipped with dephlegmator, and the hydrocarbon evolved was distilled at 85°. The hydrocarbon was washed with dilute sulfuric acid (1 : 1), then with water, and dried over potash. There resulted 9.4 g (56%) of product boiling in the range 79-81°.

It was shown spectroscopically that the product did not represent uniform cyclohexadiene-1,3, but was found to be a mixture of cyclohexadiene-1,3 and cyclohexene and benzene. Separation of this mixture by simple fractionation was a task which could not be accomplished by the authors; the authors were therefore obliged to carry out rupt-

ure of hydrogenbromide from the dibromide by means of alcoholic alkali, whereupon it became evident that the yield of hydrocarbon is considerably lower, but the product is more uniform. 100 g of dibromocyclohexane was added in portions to a boiling solution of potassium hydroxide (60 g of potassium hydroxide in 315 ml of alcohol); reaction was accompanied by spontaneous heat evolution. After completion of addition of the dibromide, heating was carried out for 4 hours. The solution was filtered off from the potassium bromide precipitate, the filtrate diluted with water, and extracted with ether. The ether extract was washed free of alcohol with water, the ether solution dried over potash, and the ether distilled off.

The product was fractionated under atmospheric pressure, and it passed over almost completely within the range 154-156°:

n_D^{13} 1.4590, d_7^{13} 0.9180, MR_D 37.5.

This product was ethoxycyclohexene, described by a number of investigators [3]. 27 g (52%) was obtained.

Freshly fused potassium bisulfate (5% of the weight of ethoxy derivative) was added to 27 g of ethoxycyclohexene in a flask equipped with dephlegmator, and the mixture heated. The distillate was collected up to 90°, washed with water and the hydrocarbon which separated as a layer was dried over potash.

During fractionation, 14 g (82%) of fraction resulted:

B.p. 79-80°, n_D^{13} 1.4760, d_4^{13} 0.8400.

Judging from the constants [4,5], this product was taken to be pure cyclohexadiene-1,3.

Bromination of Cyclohexadiene-1,3. The calculated amount of bromine in chloroform (1 : 1) was added, with ice cooling, to a chloroform solution of cyclohexadiene-1,3 (1 : 1). The reaction mixture was washed with a dilute solution of sodium sulfite, then with water, and dried over calcium chloride. The chloroform was distilled off in vacuo. After distilling off the chloroform, the remaining oil was cooled; crystals precipitated from the oil, with varied melting points, depending upon conditions under which the solvent was distilled off. If the solvent was distilled off with heat, then the precipitated crystals possessed a m.p. of 96-98°, melting after recrystallization at 99-100°. If the solvent was distilled off in vacuo without heat, then the resulting crystals had a m.p. of 58-62°, with m.p. 64-66° after recrystallization. The oil which did not crystallize, after prolonged standing precipitated crystals which also melted at 64-66°.

Zelinsky [4], Crossley [5], Harries [6], Farmer and Scott [7] attribute the structure 1,4-dibromocyclohexene--2 to the dibromide with m.p. 99-100°, 105° and 108°, and the structure 1,2-dibromocyclohexene-3 to the dibromide with m.p. 64-68°.

It was established by the authors that 1,2-dibromocyclohexene-3, with m.p. 64-66°, yields two atoms of bromine with zinc dust when heated in dioxane, and converts into the cyclohexadiene-1,3. Under such conditions, the 1,4-dibromocyclohexene-2, with m.p. 99-100°, does not react with zinc dust at all, but in boiling xylene gives up both bromine atoms to metallic sodium, and also converts into cyclohexadiene-1,3. These facts are additional proof of the structure for each dibromide which the above-indicated authors have attributed to same.

Analytical data for bromine according to Carius, determination of molecular weight for the 99-100° product corresponded to the dibromide.

Attempts at a final and convincing solution of the question of structure for the dibromide of m.p. 99-100° by oxidation and hydrogenation did not give positive results. Upon oxidation with permanganate, the dibromide gave succinic acid, and upon ozonization and treatment of the ozonolysis products, only resinified products were obtained.

Hydrogenation over Raney nickel catalyst did not go.

Interaction of Metallic Sodium with 1,4-Dibromocyclohexene-2. Reaction was carried out in a flask with long dephlegmator. Three times the theoretical amount of freshly cut metallic sodium in the form of small lumps was placed in the flask. The xylene was twice distilled from metallic sodium.

In the xylene, reaction began only at the temperature of boiling xylene. Heating was discontinued, but the reaction mixture continued to boil with considerable spontaneous heat evolution for 10-15 minutes.

A fraction was collected in the range 70-90° from the reaction mixture. After fractionation of this cut on a column, 2 g of hydrocarbon was collected, which boiled at 79-80°:

n_D^{20} 1.4758, d_4^{20} 0.8380, MR_D 26.9.

For proof of structure, the hydrocarbon was condensed with maleic anhydride (m.p. 53°). 0.9 g of the hydrocarbon, 1.1 g of maleic anhydride and 2.5 ml of benzene were sealed in a test tube. 1.8 g of condensation product resulted with m.p. 141°, which coincides with the literature data [8].

SUMMARY

1. It has been established that cyclohexadiene-1,3 is formed upon interaction of 1,4-dibromocyclohexene-2 with metallic sodium.

2. It has been demonstrated that 1,4-dibromocyclohexene-2 does not react with zinc dust.

3. It has been demonstrated that for equal liklihood of formation of conjugated or of isolated bonds in a six-membered ring, formation of conjugated bonds takes preference.

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SYNTHESIS OF CYCLOPENTANOL

Ya. M. Slobodin M. V. Blinova and N. I. Devyatova

Synthesis of cyclopentanol is carried out by reduction of readily accessible cyclopentanone by various procedures. However, this reaction is very frequently accompanied by considerable condensation of the ketone, as the result of which yields of the alcohol are usually low.

Wislicenus [1] prepared cyclopentanol in low yield by reducing cyclopentanone with sodium in moist ether. Venus-Danilova [2] demonstrated that to increase the yields of cyclopentanol it is necessary to free very thoroughly the ether from traces of ethyl alcohol. She was able to increase yields of cyclopentanol to 48-50%. Yields of the alcohol are not very constant, however. The reaction of tertiary butyl magnesium chloride with cyclopentanone leads to formation of cyclopentanol in yields of 11-60% [2]. Upon hydrogenation of the ketone over nickel at 125°, a complex mixture of products is formed, containing a small amount of cyclopentanol [3]. Hydrogenation over platinum catalyst in ether solution leads to formation of cyclopentane, cyclopentanol and other products [4]. According to the literature directions, cyclopentanol can be obtained in high yield by hydrogenation of the ketone in the presence of platinum under pressure [5].

The authors have investigated various methods for reducing cyclopentanone. It has been established that cyclopentane is formed predominantly upon hydrogenation over nickel catalyst supported by kieselguhr, at 125°. Hydrogenation over copper-chromo-barium catalyst at 160-170° led to formation of cyclopentanol in yield of 15%. Ketone condensation products form for the most part. Upon reducing the ketone with sodium in moist ether, the yields of alcohol fluctuated considerably, averaging about 30%.

By reduction of cyclopentanone with aluminum isopropylate under normal conditions it is possible to obtain cyclopentanol [6] in yield of 25-30%, in which case, however, the alcohol yields are not constant but are subject to considerable fluctuations, which is related to ketone condensation which proceeds simultaneously under the reaction conditions. A detailed study of this process has indicated that the extent of ketone condensation, and hence yields of alcohol, depend considerably upon duration of ketone contact with the aluminum isopropylate. The shorter the contact time, the less the extent of ketone condensation, and hence the higher the yield of alcohol. By carrying out this reaction under the conditions described below, it is possible to increase the yields of cyclopentanol to 62-66% with satisfactory reproducibility. This makes it possible to recommend the directions below as the appropriate laboratory method for preparing cyclopentanol.

EXPERIMENTAL

Aluminum isopropylate was prepared in the flask from 27 g of aluminum and 300 ml of anhydrous isopropyl alcohol [7]. The flask was then connected to a small dephlegmator and heated on an oil bath to the start of alcohol distillation, after which a solution of 27.5 g of cyclopentanone in 500 ml of isopropyl alcohol was added to the alcoholate. Addition of the cyclopentanone solution was carried out over a period of 12 hours. Temperature of the oil bath was maintained at 115-117°. After termination of addition of the ketone, heating of the flask was continued until the last portions of distillate ceased to give a positive reaction with dinitrophenylhydrazine. The flask was cooled in ice water, after which aqueous isopropyl alcohol (250 ml of alcohol and 70 ml of water) was added. The mixture was left at room temperature for the night, and the precipitate then filtered off. The precipitate on the filter was dissolved in sulfuric acid (80 ml of sulfuric acid and 500 ml of water), the acid solution extracted with ether, and the ether extract dried over potash.

The filtrate containing isopropyl alcohol, and almost all of the cyclopentanol were fractionated. After two fractionations, two fractions were isolated with b.p. 139-142°. From the ether extract a small amount of analogous products was isolated. The yield of crude cyclopentanol was 17.5 g (62.0%).

For characteristics, the fraction boiling at 140-141° was isolated.

d_4^{20} 0.9436, n_D^{20} 1.4520, MR_D 24.59. $C_5H_{10}O$. Calculated 24.61.

Combination Dispersion Spectrum [8].

840 (3), 894 (10), 938 (1), 1000 (3 b),   1034 (5), 1072 (3), 1187 (band), 1294 (band), 1344 (1), 1398 (1),

1449 (10), 1480 (1), 2870 (10), 2921 (1·), 2961 (1ſ).

SUMMARY

A method for preparing cyclopentanol has been described.

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INVESTIGATION IN THE FIELD OF SUBSTITUTED THIOCARBAZONES

SYNTHESIS AND STUDY OF THE PROPERTIES OF ASYMMETRICAL THIOCARBAZONE DERIVATIVES

L. S. Pupko and P. S. Pelkis

Diphenylthiocarbazone (dithizone) (I) is widely used as an analytical reagent. With respect to this fact, the synthesis and investigation of the properties of its derivatives and analogs is of special interest.

Such investigations have led to the discovery of new organic reagents possessing certain properties differing from dithizone, and to a clarification of the effect of various substituents upon the analytical properties of such compounds [1-5].

$$C_6H_5-NH-NH > C=S; \qquad RNH-NH > C=S.$$
$$C_6H_5-N=N \qquad\qquad R'N=N$$
$$(I) \qquad\qquad\qquad (II)$$
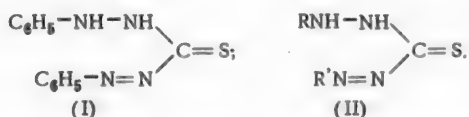
Unsymmetrical thiocarbazones of the type (II) have not been synthesized up to the present time due to the ab- of a method for their synthesis. In 1953, Irving and Bell attempted to prepare the unsymmetrical 1-phenyl-5-s-5-(2,4-dibromophenyl)-thiocarbazone by bromination of 1-phenyl-5-(2,4-dibromophenyl)-pharmazane and further action of the bromo derivative with sodium hydrosulfide. Due to insolubility of the resulting tribromoderivative, the authors failed to prepare the thiocarbazone [6].

The present authors have developed a method which permits preparation of a number of unsymmetrical thiocarbazones, among them 1-phenyl-(2,4-dibromophenyl)-thiocarbazone.

We were interested in the problems of how unsymmetrical thiocarbazones react with various cations, how disruption of the symmetry affects the character of the thiocarbazone absorption curves and their complexes with cations, and to what extent unsymmetrical thiocarbazones are stable to oxidation. The present work is devoted to a study of these problems.

The authors were not able to obtain unsymmetrical thiocarbazones according to the Fischer method [7] nor by the formazyl method [8], nor by interaction of arylhydrazines with thiophosgene. Only by the Bamberger method [8] for synthesis of symmetrical thiocarbazones, as modified by the authors, separating the nitroformaldehydrazone [9] in pure form, were the authors able to prepare the pure unsymmetrical thiocarbazones from the conjugation product between the diazonium salt and an alkaline solution of nitromethane.
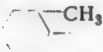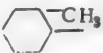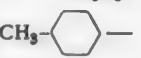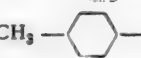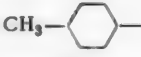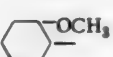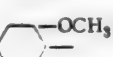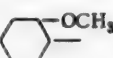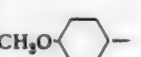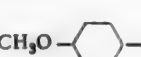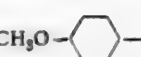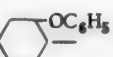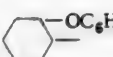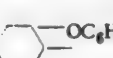
Unsymmetrical thiocarbazones, not described in the literature up to the present time, were prepared according to the following scheme:

$$C_6H_5NH_2 \xrightarrow{HNO_2} C_6H_5N=NCl \xrightarrow{CH_3NO_2} \underset{\text{Separates in the pure form}}{C_6H_5N=N-CH_2NO_2} \xrightarrow{ArN=NCl} C_6H_5N=NCH(NO_2)N=NAr \rightarrow$$

$$\xrightarrow[C_2H_5OH]{(NH_4)_2S} \underset{NH_2\ SH}{C_6H_5NHNH-C-NHNHAr} \xrightarrow{-NH_3} \underset{ArNHNH}{C_6H_5NHNH} C=S \xrightarrow{O} \underset{ArNH-NH}{C_6H_5N=N} C=S \ \text{or} \ \underset{ArN=N}{C_6H_5NH-NH} C=S$$
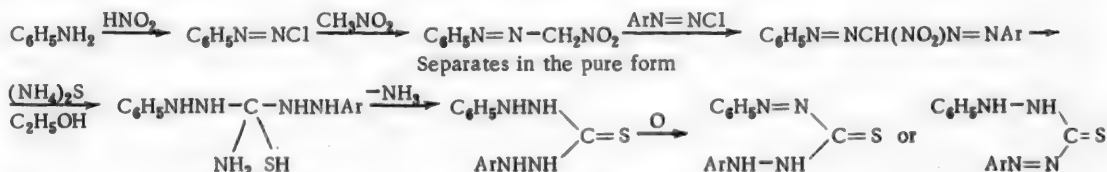
The question of double bond location presented another problem of interest.

In the table there are presented absorption maxima and molar extinction coefficients for the unsymmetrical thiocarbazones (II) synthesized by the present authors, and their corresponding symmetrical thiocarbazones. The symmetrical thiocarbazones were synthesized by methods described in the literature, and investigated spectrophotometrically by the authors for the first time. Thiocarbazones are soluble in benzene, chloroform and carbon tetrachloride with a green coloration.

Absorption curves for the thiocarbazones (Figs. 1, 2 and 3) were determined on a Bellinham and Stanley spectrophotometer. For the measurements, solutions of the dyes in benzene were taken of concentration 6.6×10^{-5} moles per liter.

No.	R	R'	ϵ_{max}	λ_1	λ_2
1	C_6H_5	C_6H_5 [10]	$7.9 \cdot 10^4$	450	620
2	C_6H_5	(o-CH₃)	$7.5 \cdot 10^4$	460	626
3	(o-CH₃)	(CH₃) [2]	$12.1 \cdot 10^4$	472	633
4	(CH₃)	(CH₃)	$12.8 \cdot 10^4$	464	635
5	C_6H_5	(CH₃) [2]	$9.6 \cdot 10^4$	455	625
6	(CH₃)	(CH₃)	$14.4 \cdot 10^4$	465	631
7	C_6H_5	(CH₃)	$11.2 \cdot 10^4$	458	626
8	(OCH₃)	(OCH₃) [5]	$16.8 \cdot 10^4$	486	659
9	C_6H_5	(OCH₃)	$13.8 \cdot 10^4$	470	640
10	CH₃O–	CH₃O– [5]	$17.3 \cdot 10^4$	476	646
11	C_6H_5	CH₃O–	$11.1 \cdot 10^4$	470	632
12	(OC₆H₅)	(OC₆H₅) [5]	$16.8 \cdot 10^4$	490	650
13	C_6H_5	(OC₆H₅)	$11.7 \cdot 10^4$	460	635
14	C_6H_5	Br–(Br)	$3.8 \cdot 10^4$	435	630
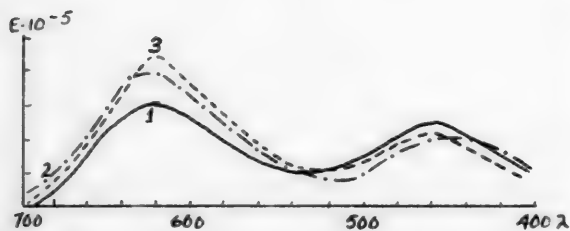
Fig. 1.
1) 1-phenyl-5-(o-tolyl)-thiocarbazone;
2) 1-phenyl-5-(m-tolyl)-thiocarbazone;
3) 1-phenyl-5-(p-tolyl)-thiocarbazone.
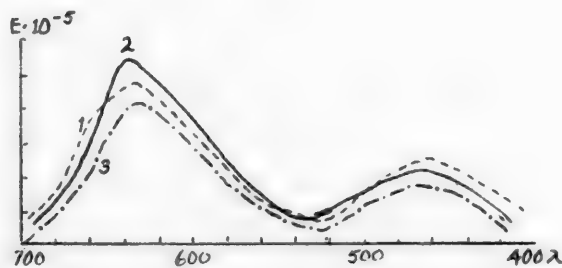
Fig. 2.
1) 1-phenyl-5-(phenoxyphenyl)-thiocarbazone;
2) 1-phenyl-5-(o-methoxyphenyl)-thiocarbazone;
3) 1-phenyl-5-(m-methoxyphenyl)-thiocarbazone.

As can be seen from the Table, the absorption maxima for all unsymmetrical thiocarbazones are shifted to the long wave-length range, as compared with the absorption maxima for dithizone. If one compares the positions of the long wave absorption maxima for the unsymmetrical thiocarbazones with the absorption maxima for the corresponding symmetrical derivatives, it will be found that the maxima for unsymmetrical lie for the most part in the middle between the maxima for the symmetrical.
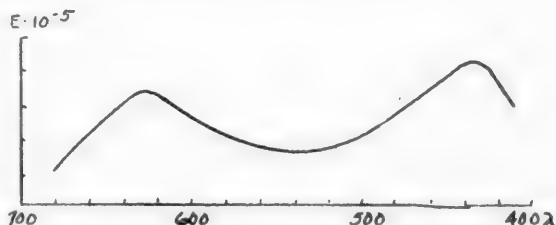
All unsymmetrical thiocarbazones give intra-complex compounds with Pb, Hg, Zn and Ag cations, soluble in organic solvents.

On the absorption curves for these intracomplex compounds, measured in benzene, are two maxima in the short wave range, shifted in the direction of the long waves as compared with the maxima for the intra-complex of dithizone with the same cation.

Fig. 3. 1-Phenyl-5-(2,4-dibromophenyl)-thiocarbazone.

EXPERIMENTAL

Synthesis of Nitroformaldehydrazone. Prepared according to Bamberger [9]. Fine crystals, orange in color, with m.p. 87-91°. Yield was 4.9 g (29.6 %).

1-Phenyl-5-(o-phenoxyphenyl)-thiocarbazone. 1.34 g of o-phenoxyaniline [5] was diazotized by dissolving in 0.79 g of concentrated hydrochloric acid and 4 ml of water with addition of 0.6 g of sodium nitrite in 2 ml of water, at 0°. 0.42 g of nitroformaldehydrazone dissolved in 35 ml of ethyl alcohol was added to the resulting diazo solution, and 30 ml of water then added to the reaction mixture. The formazyl derivative, dark-red in color, precipitated. The precipitate was filtered, washed with water, alcohol, and ether. Yield was 0.8 g (31.7%).

The formazyl derivative was suspended in a small amount of methyl alcohol, and gaseous ammonia and hydrogen sulfide passed through the alcoholic solution until the red color of the solution had turned to yellow. The solution was poured into ice water and the precipitated light-yellow solid filtered, washed with water, and dried at room temperature. The precipitate was treated with 2.5% alcoholic solution of potassium hydroxide and the solution filtered. The thiocarbazone was precipitated from solution with 1% H_2SO_4 from an alcoholic solution of potassium hydroxide.

Fine, green-black crystals with metallic lustre. M.p. 133-134° (decomp.). Yield was 0.3 g (12%).

Found %: N 15.90, 15.73. $C_{19}H_{16}ON_4S$. Calculated %: N 16.09.

1-Phenyl-5-(o-tolyl)-thiocarbazone and 1-phenyl-5-(m-tolyl)-thiocarbazone were synthesized under conditions similar to that for the 1-phenyl-5-(o-phenoxyphenyl)-thiocarbazone.

1-Phenyl-5-(o-tolyl)-thiocarbazone. 0.8 g of o-toluidine was taken. The red formazyl derivative resulted. After 3 precipitations, the thiocarbazone was in the form of dark-red needles with metallic lustre. M.p. was 129-130° (decomp.). Yield was 0.25 g (12.4%).

Found %: N 20.84, 20.58. $C_{14}H_{14}N_4S$. Calculated %: N 20.74.

1-Phenyl-5-(m-tolyl)-thiocarbazone. 0.8 g of m-toluidine was taken. The resulting thiocarbazone was precipitated twice and isolated as dark-green, needle crystals with metallic lustre. M.p. 127-128° (decomp.). Yield was 0.27 g (13.4%).
Found %: N 20.43, 20.56. $C_{14}H_{14}N_4S$. Calculated %: N 20.74.

1-Phenyl-5-(p-tolyl)-thiocarbazone. 0.8 g of p- toluidine was taken. The resulting thiocarbazone was in the form of dark green crystals of metallic luster. M.p. 132-13° (decomp.). Yield of purified thiocarbazone was 0.? g (1.'.9%).

Found %: N 20.85, 20.31. $C_{14}H_{14}N_4S$. Calculated %: N 20.74.

1-Phenyl-5-(o-anisyl)-thiocarbazone. 1.17 g of o-anisidine was taken. The resulting thiocarbazone was purified by four-fold precipitation and isolation in the form of brown needles with metallic luster. M.p. was 137-138°. (decomp.). Yield was 0.25 g (9.2%).
Found %: N 19.20, 19.35. $C_{14}H_{14}ON_4S$. Calculated %: N 19.59.

1-Phenyl-5-(p-anisyl)-thiocarbazone. 1.17 g p-anisidine. After 3 precipitations, thiocarbazone, dark-green crystals with metallic luster, m.p. 139-140 (decomp.). Yield 0.3 g (11%).
Found %: N 19.51, 19.40. $C_{14}H_{14}ON_4S$. Calculated %: N 19.59.

1-Phenyl-5-(2,4-dibromophenyl)-thiocarbazone. 1.25 g of 2,4-dibromoaniline dissolved in 2.5 g of fuming nitric acid and 4 ml of water was diazotized with 0.37 g of sodium nitrite in 2 ml of water at 0-2°. The resulting diazo solution was added to a mixture of 25 g of crystalline sodium acetate and 12.5 ml of glacial acetic acid, with continuous stirring. 0.15 g of the hydrazone diluted in 5 ml of methyl alcohol was then added to the mixture. The solution became red instantaneously, and the formazyl derivative precipitated — dark-red crystals. Stirring was continued for 1 hours. The precipitate was filtered, washed with water, methyl alcohol and ether.

Reduction of the nitroformazyl and oxidation of the resulting thiocarbazide to the 1-phenyl-5-(2,4-dibromophenyl)-thiocarbazone was carried out according to the procedure given for 1-phenyl-5-(o-phenoxyphenyl)-thiocarbazone. The thiocarbazone was in the form of red crystals with metallic lustre. M.p. 99° (decomp.). Yield was 0.26 g (11%).

Found %: N 13.29, 13.34. $C_{13}H_{10}N_4Br_2S$. Calculated %: N 13.49.

SUMMARY

A method for synthesizing thiocarbazones with two different aryl groups has been developed. 7 unsymmetrical thiocarbazones have been prepared. Their absorption curves have been made.

It has been found that values for the absorption maxima of unsymmetrical thiocarbazones are equal to the arithmetic mean of the maxima for the two corresponding paris of symmetrical thiocarbazones.

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CONVERSION OF 3,4-DIMETHYLFURANIDINE INTO
3,4-DIMETHYLTHIOPHANE AND 3,4-DIMETHYLPYRROLIDINE. XLII.

Yu. K. Yuryev and G. Ya. Kontradyeva

Detailed study of the catalytic conversion of furanidine homologs into thiophane and pyrrolidine homologs, described in previous communications [1,2] made it possible to establish that the duration of these reactions depends chiefly upon the molecular weight and structure of the initial oxide. Where mono- and dialkylfuranidine isomers of identical molecular weight are concerned, the yield of ultimate conversion products depends upon the location of the alkyl radicals in the furanidine molecule. Alkyl substitutes in the α-carbon atom of the furanidine ring cause a considerable decline in alkylthiophane and alkylpyrrolidine yields relative to that of thiophane proper and, correspondingly, of pyrrolidine. When these same substitutes are in the β-position, they affect, but to a much more limited degree, the reactions in which sulfur and nitrogen-containing heterocyclic compounds are formed from their oxygen-containing analogs. Thus, for example, 3-methyl-furanidine converts to 3-methylthiophane with a 81% yield, while 2-methyl furanidine gives a 69% yield of 2-methylthiophane; 3,3-dimethylfuranidine gives a 73% yield of 3,3-dimethylthiophane, and its isomers, 2,4- and 2,2-dimethylfuranidine give 2,4- and 2,2-dimethylthiophanes in yields of 58% and 27% respectively.

The present work will show that 3,4-dimethylfuranidine, in which both methyl groups are in the beta position, as they are in 3,3-dimethylfuranidine, readily converts, in the conditions of catalytic conversion of oxygen-containing heterocyclics into rings with other hetero-atoms, into the corresponding compounds of the thiophane and pyrrolidine series — 3,4-dimethylthiophane (71% yield) and, correspondingly, 3,4-dimethylpyrrolidine (42% yield), hitherto not described in the literature.
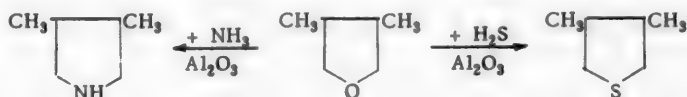
We obtained 3,4-dimethylfuranidine, also not described in the literature, by dehydration of 2,3-dimethylbutanediol-1,4, which, in its turn, had been obtained by reduction of sodium in triethyl ester butane-2,2,3-tricarboxylic acid alcohol. Longinov [3], it is known, described the reduction of Na in tricarboxylic ether alcohols of the $(COOR_1)_2C(R)-$ $-CH_2COOR_1$, type, resulting in the production of substituted tetramethyleneglycol having, as a general formula $CH_2OH-CH(R)-CH_2-CH_2OH$.

The mechanism of this reaction was studied, somewhat later, by Dzirkal, a pupil of Longinov. Studying the analogous cleavage of substituted malonic esters, Dzirkal showed that, when reacted with hydrogen, one carboethoxyl group splits off at the moment that $RHC(COOR_1)_2$ separates from the ester, and a monocarboxylic acid ester is formed, which is then reduced in the usual way [4]. The dicarboxylic acid esters and then the corresponding glycols are obtained analogously from the tricarbonic acid esters. There is no reference in the literature to reduction of the tricarboxylic esters of the general formula $(COOR_1)_2(R)C-CH(R)-COOR_1$, although our reduction of the triethyl ester of butane-2,2,3-tricarboxylic acid demonstrated that it follows the same course described by Longinov and Dzirkal for the conversion of monoalkyltricarboxylic tri- or monoalkyldicarboxylic esters with two carbalkoxyl groups at the same carbon atom, and results in the corresponding butanediol-1,4, substituted in positions 2 and 3.

EXPERIMENTAL

Synthesis of 3,4-dimethylfuranidine

The complete course of synthesis of 3,4-dimethylfuranidine performed in the present study included the following stages:

$$C_2H_5COOH \xrightarrow[\text{2) } + C_2H_5OH]{\text{1) } + Br_2} CH_3CHBrCOOC_2H_5 \xrightarrow{+ NaCH(COOC_2H_5)_2}$$

$$\begin{array}{c} CH_3 \\ | \\ CH\text{————}CHCOOC_2H_5 \\ | \qquad\qquad | \\ COOC_2H_5 \quad COOC_2H_5 \end{array} \longrightarrow$$

$$\xrightarrow[\text{2) } + CH_3I]{\text{1) } + Na} \begin{array}{c} CH_3 \qquad CH_3 \\ | \qquad\quad | \\ CH\text{————}C\text{—}COOC_2H_5 \\ | \qquad\qquad | \\ COOC_2H_5 \quad COOC_2H_5 \end{array} \xrightarrow[+ C_2H_5OH]{+ Na} \begin{array}{c} CH_3 \quad CH_3 \\ | \qquad\; | \\ CH\text{————}CH \\ | \qquad\; | \\ CH_2OH \quad CH_2OH \end{array} \longrightarrow$$
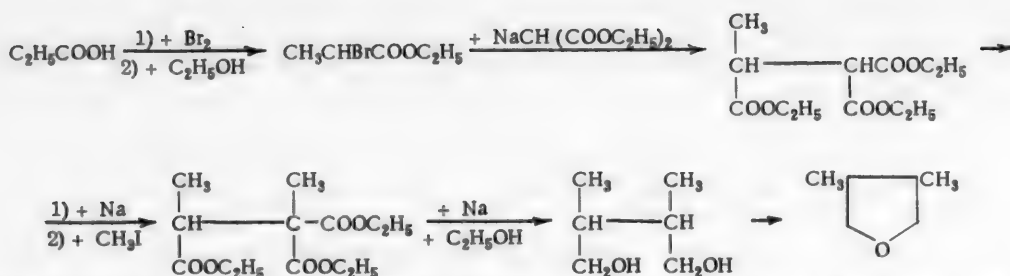
The ethyl ester of a-bromopropionic acid was obtained by the Zelinsky method [5]; b.p. 154-157° (756 mm).

Butane-2,3,3-tricarboxylic acid ethyl ester(butanetricarboxylic ester). 120 g (0.75 g/mole) malonic ester, and then, by drops and with stirring, 136 g (0.75 mole) a-bromopropionic acid ester were added to an alcohol solution of sodium ethylate, composed of 18 g (0.75 g-at.) sodium in 270 ml anhydrous ethyl alcohol. The reaction mixture was heated over a bath of boiling water until a test of the solution no longer showed a neutral reaction to phenolphthalein, and was then cooled to room temperature. Another 18 g sodium was added to the cold mixture in small pieces, and, after complete solution had been obtained, 114 g (0.8 mole) methyl iodide was added from a dropping funnel. The mixture was heated, with constant stirring, for 2 hours, and then permitted to stand overnight. The alcohol was then distilled off in a vacuum (over a water bath), and water was added to the residue to dissolve the sodium bromide. After the butane-2,3,3-tricarboxylic acid ethyl ester had been removed from aqueous solution and desiccated with calcium chloride, it was distilled in a vacuum b.p. 137-139° (4 mm). Yield 140 g (66%).

Data from the literature [6]: b.p. 205-215° (125 mm).

2,3-Dimethylbutanediol-1,4. 40 g (1.74 g-at) Na, in two large chunks, was placed in a round-bottomed flask with horned adapter and copper reflux condenser; to this was added, quickly a solution of 28 g (0.102 mole) butanetricarboxylic ester in 400 ml anhydrous alcohol. At the conclusion of the vigorous reaction, an oil bath heated to 150° was placed beneath the flask, and the mixture was heated at this temperature for another 30 minutes after complete dissolution of the sodium; 20 ml water was then added and the reaction mixture boiled for another 20 minutes, upon which, after cooling by means of ice, 190 ml concentrated hydrochloric acid was added. The residue of sodium chloride was filtered and washed 3 times in 60 ml anhydrous alcohol. The combined alcohol solutions were boiled with calcined potash until the emission of water ceased and complete desiccation had been obtained. 2,3-Dimethylbutanediol-1,4 was obtained by distillation of the residue after the alcohol had been driven off in a vacuum (over a water bath):

B.p. 128-130° (12 mm), n_D^{20} 1.4563, d_4^{20} 0.9856, MR_D 32.62. $C_6H_{14}O_2$. Calculated: 32.96.
Found %: C 59.24, 59.17; H 11.80, 11.70. $C_6H_{14}O_2$. Calculated %: C 60.98; H 11.88.

Yield 4.6 g (38%).
2,3-Dimethylbutanediol-1,4 is not described in the literature.

3,4-Dimethylfuranidine. 6 g 2,3-dimethylbutanediol-1,4 and 0.6 g aluminosilicate cracking catalyst were heated at 200° in a distillation flask with a tightly-sealed branch pipe. The distillate was desiccated with calcium chloride and distilled over sodium from a flask with a dephlegmator. The 3,4-dimethylfuranidine (4 g, 78%) had the following constants:

B.p. 108.4-108.8° (760 mm), n_D^{20} 1.4183, d_4^{20} 0.8583, MR_D 29.43. $C_6H_{12}O$. Calculated: 29.35.
Found %: C 71.75, 71.77; H 12.05, 12.15. $C_6H_{12}O$. Calculated %: C 71.99; H 12.09.

3,4-Dimethylfuranidine is not described in the literature.

3,4-Dimethylthiophane

7.7 g 3,4-dimethylfuranidine was passed over aluminum oxide in a stream of hydrogen sulfide at 350°, at a rate of 0.5 ml/min. The catalyst was saturated with alkali and extracted by ether. The ether extract was desiccated with fused caustic potash. Distillation of the reaction product gave 6.4 g (71%) 3,4-dimethylthiophane:

B.p. 155.4-156° (756 mm), n_D^{20} 1.4908, d_4^{20} 0.9446, MR_D 35.55. $C_6H_{12}S$. Calculated: 35.68.
Found %: C 62.19, 62.15; H 10.68, 10.68; S 27.58, 27.56. $C_6H_{12}S$. Calculated %: C 62.00; H 10.41; S 27.59.

The derivative with $HgCl_2$ had a boiling point of 152 (from anhydrous alcohol).

3,4-Dimethylthiophane is not described in the literature.

3,4-Dimethylpyrrolidine

6 g 3,4-dimethylfuranidine was passed over activized aluminum oxide in a stream of ammonia at 315° and at a rate of 0.25 ml/ min. The flask was cooled to −40°, and at the end of the reaction it was connected to a reflux condenser and the ammonia gradually evaporated at room temperature. The residue was saturated with caustic potash and extracted by ether. After the ether had been driven off, 2.5 g (42%) 3,4-dimethylpyrrolidine was isolated by redistillation of the residue after caustic potash desiccation of the ether extract.

B.p. 121-122° (750 mm), n_D^{20} 1.4400, d_4^{20} 0.8439, MR_D 30.98. $C_6H_{13}N$. Calculated: 31.31.

Picrate: m.p. 123-124° (from alcohol).
Found %: N 17.02, 17.42. $C_{12}H_{16}O_7N_4$. Calculated %: N 17.03.

3,4-Dimethylpyrrolidine is not described in the literature.

SUMMARY

1. 3,4-Dimethylfuranidine, the synthesis of which is described for the first time in this study, converts smoothly to 3,4-dimethylthiophane (71% yield) and 3,4-dimethylpyrrolidine (42% yield) in conditions of catalytic conversion of oxygen-containing heterocyclics into rings with other hetero-atoms.

2. The conversions of 3,4-dimethylfuranidine described proceeded in a manner analogous to the conversion of 3,3-dimethylfuranidine; the similarity of conduct of these γ-oxide isomers confirms the concept that alkyl substitutes at the β-carbon atom of the furanidine ring, affect but weakly the course of catalytic conversion into nitrogen and sulfur-containing heterocyclic compounds.

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5) See Consultants Bureau English translation, page 883.

SYNTHESIS OF γ-FORMYLPYRIDINE AND ISONICITINIC ACID

M. V. Rubtsov, E. S. Nikitskaya and A. D. Yanina

Oxidation of the appropriate   methyl derivatives of selenium dioxide readily produces quinoline aldehydes [1]. This reaction is most frequently performed in xylol or without a solvent.

With regard to the pyridine aldehydes, there is an indication in the literature that they cannot be successfully obtained by an analogous process from the appropriate methyl derivatives, as the oxidation process does not end at the aldehyde stage, but proceeds to the production of pyridine carboxylic acids.

We questioned this conclusion. We decided to attempt to select conditions under which oxidation of the methyl derivatives by selenium dioxide would result in production of the corresponding aldehydes. γ-Formylpyridine was the first to engage our interest, as this compound is of considerable importance to the synthesis of an entire series of pyridine γ-derivatives, and our interest was heightened by the fact that no convenient method of obtaining it had been described in the literature [4].

The substance with which we began was the β-picoline fraction, freed of its a,a-lutidine, and constituting a mixture of β-picoline (about 60 %) and   γ-picoline (about 40%).

Our experiments showed that treatment of this mixture with selenium dioxide results in selective oxidation of γ-picoline with the formation of γ-formylpyridine and isonicotinic acid.

When 1 mole of selenium dioxide was reacted with 1 mole of γ-picoline in dry toluol, about 13% γ-formyl-pyridine and about 33% isonicotinic acid was produced. When a doubled quantity of selenium dioxide was used in the reaction, only isonicotinic acid was formed, with a yield of up to 75%. Approximately the same results were obtained with oxidation in xylol. The isonicotinic acid was precipitated with the selenium, and the γ-formylpyridine remained in solution in the toluol, from which it was readily isolated in the form of its bisulfite derivative. Oxidation in organic solvents — toluol or xylol — proceeds rapidly and requires only an hour or two. Oxidation proceeds even more rapidly without a solvent, but it results in severe resinification of the reaction mass. It is of interest to note that oxidation in an aqueous medium resulted in the production only of isonicotinic acid, regardless of the quantity of selenium dioxide employed. Under appropriate conditions, the acid yield attained 80%.

Oxidation in water goes slower than in an organic solvent, is concluded in six hours, and gives good quality isonicotinic acid not requiring further purification. Moreover, oxidation may be conducted in water even in the presence of a,a-lutidine, as this compound does not oxidize under these conditions.

The aqueous oxidation method permits the use as oxidizing agent of 50% selenic acid, obtained by processing sulfuric acid production wastes.

EXPERIMENTAL

I. Production of γ-formylpyridine

Oxidation of γ-picoline. 20 g selenium dioxide was gradually added, with vigorous stirring, to a mixture of 52.5 g β-picoline fraction from which the a,a-lutidine had been removed and 65 ml dry toluol, heated to boiling (120°). The reaction mass was heated and boiled for two hours(constant stirring). During this process, the temperature gradually dropped to 97°. At the conclusion of the reaction, the mass was cooled and the deposit of selenium and isonicotinic acid was filtered, washed twice in 20 ml toluol, and the toluol wash mixed with the main filtrate.

Isolation of γ-formylpyridine. The toluol filtrate, containing the γ-formylpyridine, was transferred to a glass to which 15 ml of a 50% sodium bisulfite solution was added, the whole cooled to 0°, stirred until formation of a viscous mass at the bottom of the glass, the liquid poured off and 50 ml alcohol added to the residue. It was then carefully mixed, filtered, washed in 15 ml alcohol and dried in air. The product was 7.6 g impure sodium salt of γ-pyridylhydroxymethanesulfonic acid, from which 3.02 g γ-formylpyridine was obtained by the method described above [5]. The yield was 12.7% based on   γ-picoline.

Isolation of isonicotinic acid. The precipitate, containing metallic selenium and isonicotinic acid, was gradu-

ally poured into 75 ml of a 15% sodium carbonate solution, constant stirring. When this was done, the selenium was filtered out of the solution, washed in 30 ml water, and the wash water was mixed with the filtrate. The filtrate, consisting of an isonicotinic acid sodium salt solution, was treated with activated carbon and filtered, the clear, colorless solution yielding isonicotinic acid when acetic acid was added. 9.27 g isonicotinic acid was obtained, or a 33% yield, if measured in terms of γ-picoline.

12.9 g metallic selenium was obtained (91%).

II. Production of isonicotinic acid.

Oxidation in an organic solvent. 193.5 g selenium dioxide was added, bit by bit, but steadily, in the course of 30 to 45 minutes, to a vigorously-stirred mixture of 180 g β-picoline fraction freed of a,a-lutidine, with 120 ml dry xylol, heated to boiling (140°). The reaction mass was heated for an hour at boiling point, during which its temperature fell to 105-108°. The mass was then cooled, and the precipitate filtered and washed in 200 ml water and 50 ml alcohol. The gray precipitate obtained, consisting of a mixture of selenium and isonicotinic acid, was processed as above. The product was 71.4 g isonicotinic acid (75 %) with m.p. 306-308° (in a sealed capillary tube) and 126 g metallic selenium (91.5%).

Oxidation in an aqueous medium. 387 g of a 50% aqueous solution of selenium dioxide was added from a dropping funnel, with stirring, to 180 g β-picoline fraction freed of its a,a-lutidine and heated to boiling (138-140°). This was done at a rate that enabled the reaction mass to boil evenly. The temperature of boiling gradually dropped to 104-105°. After all the selenium dioxide solution was added, the reaction mass was boiled for another six hours, after which the water and β-picoline was driven off. This was done while stirring. 180 ml water was added to the dry residue, mixed until a homogeneous mass was formed, and filtered. Further processing was the same as that described above. The yield of isonicotinic acid was 76 g, or 80%, measured in terms of γ-picoline. The selenium yield was 126 g (91.5%).

SUMMARY

1. Conditions were discovered for the production of γ-formylpyridine by selective oxidation of γ-picoline by selenium dioxide in the presence of β-picoline.

2. Two methods of producing isonicotinic acid were developed which make it possible to obtain a 75-80% yield of this compound, measured in terms of γ-picoline.

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• T. p. = C.B. Translation pagination.

SYNTHESIS AND PROPERTIES OF CERTAIN BENZIMIDAZOLE DERIVATIVES

I. REACTION OF 1,2,4-TRIAMINOBENZENE WITH CARBOXYLIC ACIDS

B. A. Porai-Koshits and G. M. Kharkharova

This communication is devoted to the study of the reaction of 1,2,4-triaminobenzene with carboxylic acids, and also to investigation of the properties of 5-aminoderivatives of benzimidazole. Synthesis of the latter was undertaken at the suggestion of N. V. Lazarev with the purpose of studying their pharmacological action.

It is known that [2] lengthy boiling of the free base 1,2,4-triaminobenzene with formic or acetic acid will produce, respectively, 5-amino-and 2-methyl-5-aminobenzimidazole (I and II)
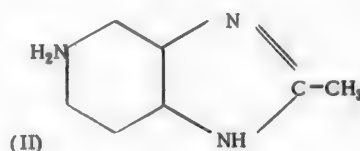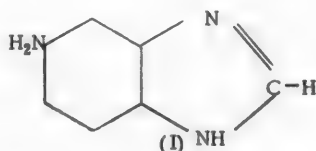
As we have demonstrated, these compounds are also readily prepared by boiling 1,2,4-triaminobenzene [1] dichloride with the acids mentioned above.

We found no references to the condensation of 1,2,4-triaminobenzene with aromatic (i.e., benzoic) and aliphatic-aromatic (phenylacetic and hydrocinammic) acids. However, reaction of these acids with the ortho-diamines of the benzene series proceeds rather smoothly in tubes under pressure, in the presence of hydrochloric acid [3,4].

The concentration of the latter to be used depends upon the basicity of the ortho-diamine: the greater the basicity, the lower the concentration of hydrochloric acid required to attain the maximum benzimidazole derivative yield [3,4].

The basicity of 1,2,4-triaminobenzene ($k = 10^{-7.9}$), is considerably higher than that of 3,4-toluylene diamine ($k = 10^{-9.0}$), o-phenylene diamine ($k = 10^{-9.15}$) and 3,4-diaminochlorobenzene ($k = 10^{-9.7}$) [5].
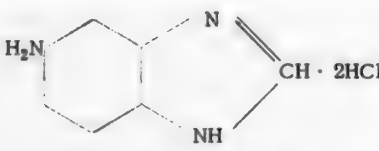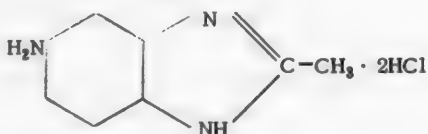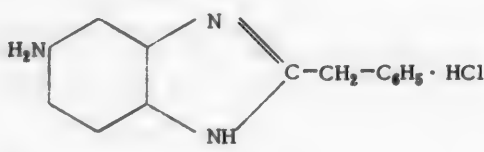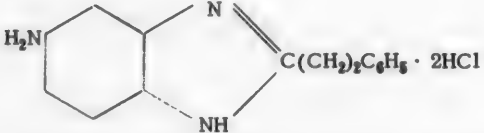
However, to obtain the maximum reaction product yield from carboxylic acids and 1,2,4-triaminobenzene a higher concentration of hydrochloric acid is needed than for the attainment of the highest yield of condensation products of these acids with the given ortho-diamines. At low concentrations (5-15 %) of hydrochloric acid, 1,2,4-triaminobenzene reacts with benzoic and hydrocinnamic acids to give a negligible yield of 2-phenyl-5-amino- (III) and 2-(β-phenylethyl)-5-amino-benzimidazole (IV) chlorohydrates:
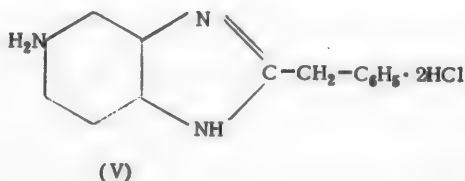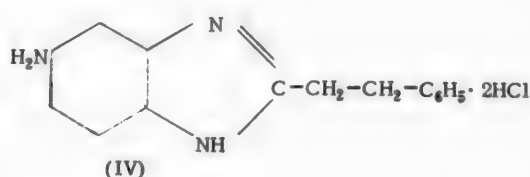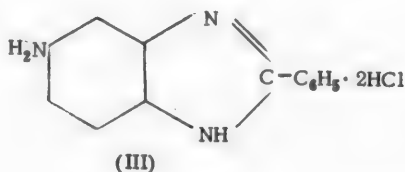
Concentration of this compound with phenylacetic acid gives much better results under these conditions. Thus, 2-benzyl-5-amino-benzimidazole chlorohydrate (V) was obtained in a yield of 25% of the theoretical in the presence of 15% hydrochloric acid. Detailed study of this reaction revealed that the yield of (V) depended to a considerable degree not only on the hydrochloric acid concentration, but on the temperature and the duration of the heating of the reaction mass. The optimum yield (74-80%) of 2-benzyl-5-amino-benzimidazole (V) in the presence of 30-35% hydrochloric acid was obtained by heating the initial products in tubes at 150-160° under pressure for seven hours. Lower duration and temperature of heating of the reaction mass led to a drop in yield, while an increase in these factors led to a reduction in the quality of the final product. These were the conditions in which 1,2,4-triaminobenzene was reacted with hydrocinammic (60-70%) and benzoic (10-15%) acids.
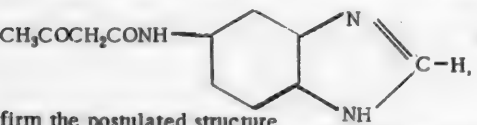
2-Benzyl-5-amino-(V) and 2-(β-phenylethyl)-5-amino-benzimidazole (IV) chlorides were first obtained by us. Their structure was determined by the process of synthesis and was confirmed by potentiometric titration by a 0.1 N solution of caustic soda, and also by combustion with nitrogen. Considerable difficulties were encountered in freeing the 5-amino derivatives of benzimidazole from impurities. All the sulfides (I, II, III, IV, V) were readily soluble in water, slightly soluble in alcohol and virtually insoluble in ether and benzene. Their constants of basicity were low, as were their pH in aqueous solution (Table 1). The most basic of the amines adduced in Table 1 was, as might have been expected, 2-methyl-(II) and 2-(β-phenylethyl)-5-amino-benzimidazole (IV). In the latter instance the phenyl radical virtually failed to affect the basicity of the benzimidazole derivative.

TABLE 1

pH 0.02 N of the Solutions and Basicity Constants of Certain 5-Amino Derivatives of Benzmidazole (I, II, III and IV)

| No.	Formula	pH of 0.02 N solution	Basicity K at 25°
1	H_2N ... $CH \cdot 2HCl$ (N, NH)	1.5−2.0	$10^{-7.4}$
2	H_2N ... $C-CH_3 \cdot 2HCl$ (N, NH)	2.5−2.8	$10^{-7.2}$
3	H_2N ... $C-CH_2-C_6H_5 \cdot HCl$ (N, NH)	3.0−3.1 •••	$10^{-7.4}$
4	H_2N ... $C(CH_2)_2C_6H_5 \cdot 2HCl$ (N, NH)	3.15−3.2	$10^{-7.2}$

These amines are readily acylated* and diazotized. Their diazo solutions combine readily with various azo components.•• Thus, for example, they form a crimson dye with Azotol A.

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* When 5-amino-benzimidazole is reacted with diketene it forms acetoacetyl-5-amino-benzimidazole

CH_3COCH_2CONH ... $C-H$, (N, NH) which decomposes at 204-205°. Results of analysis for nitrogen confirm the postulated structure.

•• 5-Diazo-benzimidazole combines with salicylic acid to form 5-(p-oxy-m-carboxy-benzeneazo)-benzimidazole a yellow azo compound with a melting point of 272-273°. ••• The pH of 1 to 3% solutions falls from 3 to 2.7.

We obtained interesting findings when we compared the constants of basicity of the above-mentioned o-phenyl-enediamine derivatives to their reactive capacities in concentrated hydrochloric acid. We observed that the yields of the condensation products of phenylacetic acid and 3,4-diaminochlorobenzene, o-phenylenediamine and 3,4-tol-uylenediamine (VI, VII, VIII) declined inversely to the rise in basicity constant of orthodiamines (Table 5). 1,2,4-Triaminobenzene behaves differently under these conditions, however. It condenses with phenylacetic acid much more readily than does 3,4-toluylenediamine, although its basicity is considerably higher than that of the latter (Table 5).

(VI)   (VII)

(VIII)
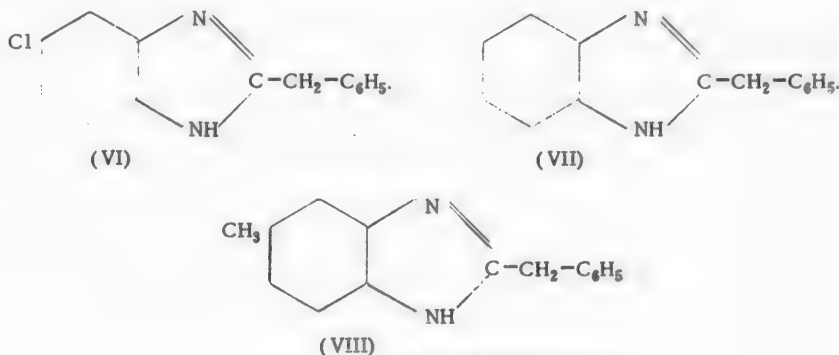
EXPERIMENTAL

1,2,4-Triaminobenzene dichloride

1,2,4-Triaminobenzene was produced analogously to the production of o-phenylenediamine [6,7] by the reduction of 4-nitro-1,3-phenylenediamine by sodium sulfide.

3 parts 4-nitro-1,3-phenylenediamine was added to an aqueous solution, filtered for impurities, consisting of 7 parts 60% melted sodium sulfide and 13 parts water. With the mixer in constant motion, the mixture was heated to 108-109°, upon which heating was interrupted for a period, as the temperature of the flask contents rose spontaneously to 110-112°. That temperature was then maintained for four hours by heating until reduction of the 4-nitro-1,3-phenylenediamine was completed. Cooling of the reaction mass proceeded at room tempearture. The 1,2,4-triami-nobenzene crystals were filtered, washed in a small amount of ice water, and with an alcohol-ether mix (1 : 1)• and dissolved in hot ethyl alcohol. The alcohol solution was filtered free of contaminants, and the 1,2,4-triaminobenzene dichloride was precipitated by twice its volume of 35% hydrochloric acid.

1,2,4-Triaminobenzene dichloride was obtained in the form of ye llow-gray needles, decomposing at 243-246° with a yield of about 80%.

0.1960 g sub.: 20.01 ml 0.1 N NaOH. $C_6H_3(NH_2)_3 \cdot 2HCl$. Calculated: 0.1 N NaOH 20.0 ml.

5-Amino-benzimidazole Dichloride

a) 19.6 g 1,2,4-triaminobenzene dichloride and 12 ml 90% cinnamic acid were heated for 8 hours over a water bath. 100 ml 15% hydrochloric acid was added after cessation of generation of gaseous hydrogen chloride (Congo paper test); the whole was then boiled for an hour, filtered free of impurities and concentrated in a vacuum until the onset of 5-amino-benzimidazole hydrochloride crystallization. After recrystallization out of 50% aqueous alcohol the yield was 35 to 40%.

b) Heating of equimolecular quantities of 1,2,4-triaminobenzene dichloride and cinnamic acid in tubes under pressure and at 160 to 170° for five hours gave a 60% yield of 5-amino-benzimidazole hydrochloride.

0.2000 g sub.: 9.08 ml 0.935 N solution $NaNO_2$. Found amine, %: 100.13.
0.1890 g sub.: 18.1 ml 0.1 N NaOH. $C_7H_7N_3 \cdot 2HCl$. Calculated: 18.2 ml 0.1 N NaOH.

The needles were gray in color, decomposed at 315 to 317°, dissolved freely in water and slightly in alcohol. They diazotized readily, and the diazo compounds combined well in an acetic acid medium, with various azo components (forming a crimson dye with Azotol A, and a yellow azo compound with salicyclic acid). These compounds decomposed upon long heating in hydrochloric acid. The pH of an 0.5% aqueous solution was 1.5-2.0.

• After crystallization out of chloroform 1,2,4-triaminobenzene melts at approximately 100° (decomposing).

5-(p-Oxy-m-carboxy-benzene-azo)-benzimidazole

3.75 g of 5-aminobenzimidazole dichloride was diazotized in the usual way [8]. The diazo solution was filtered and added to a solution of 2.88 g sodium salicylicate and 8 g soda in 35 ml water. They combined slowly. An azo compound, yellow in color, was filtered off after 3 days. The yield was 3.72 g.

The small yellow needles, with a melting point of 272-273° (from alcohol), are slightly soluble in water and 10% hydrochloric acid.

0.1076 g sub.: 18 ml N_2 (21°, 775 mm). Found %: N 19.4. $C_{14}H_{10}O_3N_4$. Calculated %: N 19.8.

Acetoacetyl-5-amino-benzimidazole

2 g 5-amino-benzimidazole hydrochloride was dissolved in 15 ml water, 4 g diketene and 8 g sodium acetate being added to this solution. The whole was mixed and gently heated over a water bath. While still warm, the solution was filtered free of the small quantity of impurities present. The precipitate deposited from the solution when it cooled was filtered, washed with water and then alcohol, desiccated and recrystallized. The yield was 1.2 g (47%).

0.0790 g sub.: 12.8 ml N_2 (20°, 764 mm). Found %: N 18.80. $C_{11}H_{11}O_2N_3$. Calculated %: N 19.80.

The needles, small, slender and colorless (from alcohol), decomposed violently at 204-205°; they were slightly soluble in cold and hot chloroform, benzene, ether, and water, but did dissolve in alkalis and acids. Combination with diazotized 1-methyl-amino-4-(p-amino-phenyl)-amino-anthraquinone results in a green dye.

2-Methyl-5-amino-benzimidazole dichloride

It was produced (a) by long heating of equimolecular quantities of acetic acid and 1,2,4-triaminobenzene hydrochloride in the presence of 14% hydrochloric acid. The reaction mass was filtered for contaminants and condensed over a water bath, giving a yield of about 30%; (b) by heating equimolecular quantities of 1,2,4-triaminobenzene and glacial acetic acid in tubes under pressure for 2 hours at 170-175°. The reaction mass was digested with 5% hydrochloric acid. The aqueous solution was filtered free of contaminants and condensed in vacuum in a stream of carbon dioxide over a water bath.

0.1747 g sub.: 7.8 ml 0.0995 N $NaNO_2$. Amine content found %: 99.0. 0.2060 g sub.: 18.4 ml 0.1 N NaOH, $C_8H_9N_3 \cdot 2HCl$. Calculated: 18.6 ml 0.1 N NaOH.

These gray needles, decomposing at 314-315°, dissolved freely in water, slightly in alcohol. The picrate melted at 213-214° (from alcohol), as indicated in the literature [2].

Reaction of 1,2,4-triaminobenzene with phenylacetic acid

a) Effect of temperature of heating upon 2-benzyl-5-amino-benzimidazole yield. Equimolecular quantities of 1,2,4-triaminobenzene (1.96 g) dichloride and phenylacetic acid (1.36 g) were heated for 7 hours in a sealed tube under pressure with 10 ml concentrated hydrochloric acid at the following temperatures: 105-110, 130, 145, 160, 180 and 200°.

The results are shown in Table 2.

b) Effect of concentration of hydrochloric acid upon 2-benzyl-5-amino-benzimidazole yield. Equimolecular quantities of 1,2,4-triaminobenzene chloride (1.96 g) and phenylacetic acid (1.36 g) were heated for 7 hours under pressure in a sealed tube to 150-160° in the presence of various concentrations of hydrochloric acid.

Table 3 shows the experimental results.

c) Effect of duration of heating upon 2-benzyl-5-amino-benzimidazole yield. Equimolecular quantities of 1,2,4-triaminobenzene chloride (1.96 g) and phenylacetic acid (1.36 g) were heated for various periods of time in a sealed tube under pressure in the presence of 35% hydrochloric acid.

Table 4 shows the experimental results.

The following gave the best yields of 2-benzyl-5-amino-benzimidazole dichloride: equimolecular quantities of 1,2,4-triaminobenzene hydrochloride (1.96 g) and phenylacetic acid (1.36 g) were heated for 7 hours in a tube under pressure in the presence of 10 ml concentrated hydrochloric acid. The tube contents were extracted by means of 150 ml water, filtered, the filtrate subjected to ether extraction to remove the phenylacetic acid and condensed to small volume in a vacuum over a water bath. After cooling the 2-benzyl-benzimidazole salt was filtered off, washed with anhydrous alcohol and ether. The average yield was 70-80%.

TABLE 2

Effect of Heating Temperature upon 2-Benzyl-5-amino-benzimidazole Chlorohydrate,(after 7 hours Heating)

No.	Heating temperature	Average yield before purification (in %)	Yield after first purification (in %)	Color of filtrate and color of substance	Remarks
1	100–110°	3–5	—	—	The initial substances were the chief products
2	120–130	71.0	64	Rose filtrate; silver-gray crystals	No contaminant dye
3	140–150	81.0	73	Rose filtrate; silver-gray crystals	Negligible quantity of black residue
4	150–160	88	79.5	Slightly bluish filtrate; silver-gray crystals	Blue dye and black residue appear
5	170–180	87.5	78.5	Blue-shaded filtrate; gray crystals	Blue dye and considerable carbon particles
6	200–210	82	74.0	Dark filtrate. Substance so dark gray as to be almost black	Much carbon and much blue dye

TABLE 3

Effect of Hydrochloric Acid Concentration Upon 2-Benzyl-5-amino-benzimidazole Yield

No.	Hydro-chloric acid concentration	Yield (%) before purification	Yield (%) after purification	Titration of 0.1006N NaNO$_2$	Amine content (%)	Remarks
1	10	60.8	54	0.296 g sub.: 12.2 ml NaNO$_2$	122	Admixture of initial triamino-benzene
2	20	62.5	57.5	0.296 g sub.: 11.3 ml NaNO$_2$	113.5	Admixture of initial triamino-benzene
3	30	71	68	0.296 g sub.: 10.3 ml NaNO$_2$	103.5	
4	35	74	72	0.296 g sub.: 10.5 ml NaNO$_2$	105.5	

TABLE 4

Effect of Duration of Heating Upon 2-Benzyl-5-amino-benzimidazole Yield (Temperature of Heating, 150-160°)

No.	Duration of heating (hrs.)	Yield (%)
1	1	63
2	3	78
3	7	79
4	12	74

0.0978 g sub.: 12 ml N$_2$(21°, 766 mm). Found %: N 14.3. 0.3286 g sub.: 22.0 ml 0.1020 N NaOH. 0.2960 g sub.: 19.7 ml 0.1020 N NaOH. 0.2364 g sub.: 15.66 ml 0.1020 N NaOH. C$_{14}$H$_{13}$N$_3$ · 2HCl. Calculated %: N 14.18; ml 0.102 N NaOH: 21.8, 19.6, 15.6. 0.2711 g sub.: 9.2 ml 0.0945 N NaNO$_2$. Found %: amine content 100.35.

The silver-gray needles, melting and decomposing at 280-285°, were readily soluble in water (14 g in 100 ml water), and slightly in 96% alcohol, readily diazotized, and the diazo compounds combined with Azo-tol A to form a crimson dye.

Decomposition followed long-term heating in hydrochloric acid. Aqueous solutions were acidic:

The pH of an 0.5% solution was 3.0-3.1, 1.0% − 2.8 - 2.9, 3.0% − 2.6 - 2.7. The basicity constant was 10$^{-7.7}$. The potentiometric titration curve showed two points of inflexion.

The picrate was yellow in color, and its melting point was 220-221°, at which deomposition occurred.

The ash content of the substance attained 0.3-0.5%.

2-(β-Phenyl-ethyl-5-amino-benzimidazole dichloride

This salt was obtained by heating equimolecular quantities (0.01 mole) of 1,2,4-triaminobenzene hydrochloride and phenylacetic acid to 150-160° for 7 hours in a sealed tube under pressure in the presence of 10 ml concentrated hydrochloric acid. The tube contents were processed as above. The yield was 2.2, 2.3, 2.1 g (about 75%).

0.2223 g sub.: 14.0 ml 0.1020 N NaOH. 0.2235 g sub.: 14.20 ml 0.1020 N NaOH. Amine content found, %: 99.5, 100.5. 0.1002 g sub.: 12.0 ml N_2 (22°, 770 mm). Found %: N 13.7. $C_{15}H_{15}N_3 \cdot 2HCl$. Calculated %: N 13.54.

These light gray flakes, which decomposed at 300°, dissolved readily in water. Aqueous solutions were acidic (0.5% solution showed a pH of 3.1-3.2). The coefficient of basicity was $10^{-7.2}$. There were two points of inflexion in the potentiometric titration curve.

2-Phenyl-5-amino-benzimidazole dichloride

This salt was obtained by reacting 1.96 g 1,2,4-triaminobenzene chlorohydrate with 1.22 g benzoic acid in the presence of 10 ml concentrated hydrochloric acid while heating to 150-160° for 7 hours under pressure.

The reaction of this acid with 1,2,4-triaminobenzene proceeded less satisfactorily than its condensation with phenylacetic and hydrocinnamic acids. The product was dirty. It did not prove possible to free this product of its contaminants completely. The yield was about 10-15%.

0.2525 g sub.: 8.6 ml 0.1006 N $NaNO_2$. Amine content found, %: 98.0.

Reaction of certain o-phenylenediamine dichloride derivatives with phenylacetic acid

Condensation of o-phenylenediamine dichlorides with 3,4-toluylenediamine, 3,4-diamino-chlorobenzene and 1,2,4-triaminobenzene with phenylacetic acid was performed as above. The data derived are presented in Table 5.

TABLE 5

Dependence of 2-Benzyl-benzimidazole Derivatives upon the Basicity of the Ortho-diamine

No.	Benzimidazole derivative	o-Diamine (salt)	Basicity of o-Diamine	Yield,%
1	2-Benzyl-5-chloro-benzimidazole	3,4-Diamino-chloro-benzene	pH 4.3 $K10^{-9.7}$	95*
2	2-Benzyl-benzimidazole	o-Phenylenediamine	pH 4.85 $K10^{-9.15}$	89
3	2-Benzyl-5-methyl-benzimidazole	3,4-Toluylenediamine	pH 5.0 $K10^{-9.0}$	68
4	2-Benzyl-5-amino-benzimidazole	1,2,4-Triaminobenzene	pH 6.1 $K10^{-7.9}$	77

2-Benzyl-5-Chlorobenzimidazole dichloride

2-Benzyl-5-chlorobenzimidazole, a base, was obtained in yield of about 95% (before purification). Melting point 171-172° (from aqueous alcohol). This base was very slightly soluble in water, but dissolved readily in alcohol. The 2-benzyl-5-chlorobenzimidazole hydrochloride was isolated by saturating an alcohol solution of the base with hydrogen chloride. The resultant small white needles, having a melting point of 248-250°, were very slightly soluble in cold water, but dissolved in alcohol.

0.2058 g sub.: 0.1051 g AgCl. 0.1831 g sub.: 0.0953 g AgCl. Found %: Cl 12.81, 12.90. $C_{14}H_{11}N_2Cl \cdot HCl$. Calculated %: Cl 12.70.

The 2-benzyl-benzimidazole and 2-benzyl-5-methylbenzimidazole dichlorides showed properties corresponding to those described in the literature [3,4].

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* From 0.01 mole o-diamine and 0.01 mole phenylacetic acid.

SUMMARY

1. The concentration of hydrochloric acid, the temperature and duration of heating strongly affect reaction of ortho-diamines with carboxylic acids in the presence of hydrochloric acid.

2. The fact was confirmed that in certain instances the less basic o-phenylenediamine derivatives provide a higher benzimidazole yield in the presence of hydrochloric acid than do the more basic. It was determined that 1,2,4-triaminobenzene   is an exception to this rule among the substances studied.

3. It was established that 1,2,4-triaminobenzene reacts with benzoic, hydrocinnamic and phenylacetic acids in the presence of concentrated hydrochloric acid to form 2-phenyl,2-benzyl- and 2-(β-phenyl-ethyl)-5-amino-benzimidazole. The latter two compounds were produced for the first time.

4. Optimum conditions for the synthesis of certain 5-amino-benzimidazole derivatives were found.

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* See Consultants Bureau English translation, page 1555.

SYNTHESIS OF SUBSTITUTED 2-AMINOMETHYLQUINUCLIDINES

M. V. Rubtsov and E. S. Nikitskaya

A previous communication [1] described the process of obtaining aminoalkyl derivatives of quinuclidine
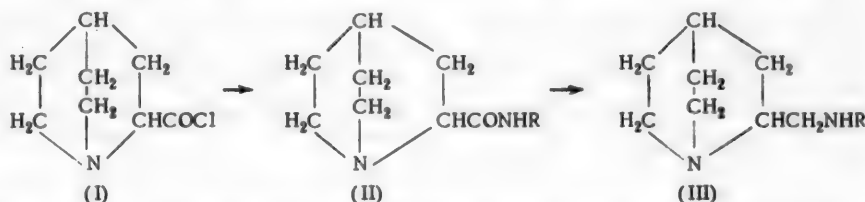

Application of this process made possible the synthesis, described in this article, of the series of compounds having (III) as their general formula, where

$$R = (C_2H_5)_2N(CH_2)_3-\underset{\underset{CH_3}{|}}{CH}-, \ (C_2H_5)_2NCH_2CH_2-, \ C_6H_5CH_2-, \ a\text{-pyridyl}, \ a\text{-thiazolyl}.$$
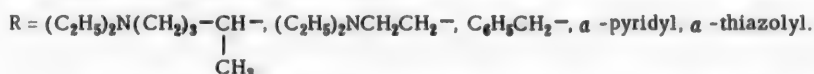
The amides (II) were obtained in an ether, benzene or pyridine medium, and they were reduced with lithium aluminum hydride in a medium of ether or ether mixed with benzene.

Attempts to obtain quinoline and acridine derivatives by an analogous procedure did not prove successful. Under the conditions described, 6-methoxy-4-aminoquinoline and 9-aminoacridine do not react with the acid chloride of 2-quinuclidinecarboxylic acid. Nor did it prove possible to obtain compound (VI) by reacting 2-aminomethylquinuclidine with 6-methoxy-4-chloroquinoline.

2-Aminomethylquinuclidine derivatives, containing the quinoline and acridine rings, were obtained by reacting 2-aminomethylquinuclidine [1] with 6-methoxy-4-sulfoquinoline and 9-phenoxyacridine as follows:
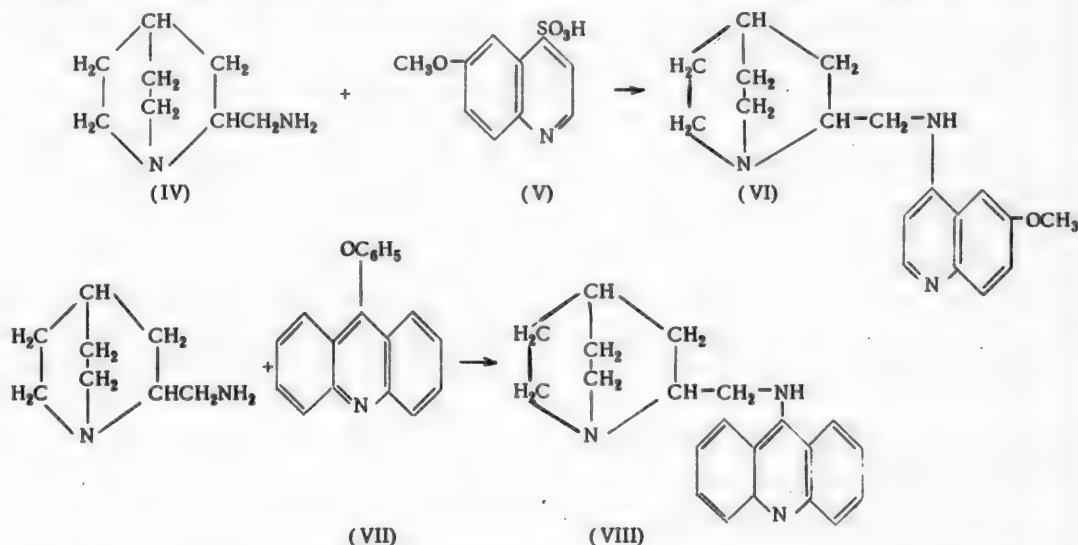
Reaction of 2-aminomethylquinuclidine with 6-methoxy-4-sulfoquinoline proceeds in an aqueous medium, while reaction with 9-phenoxyacridine proceeds in n-butyl alcohol.

EXPERIMENTAL

2-Quinuclidinecarboxylic acid diethylaminoethylamide

The acid chloride chlorine hydrate obtained as previously indicated [1] from 3 g 2-quinuclidinecarboxylic acid hydrochloride was processed in a solution of 5.45 g diethylaminoethylamine in 80 ml absolute ether and permitted to stand for 2 hours. 3 g substance (77%) was obtained with a b.p. of 170 to 180° at 7 mm.

It was a colorless oily liquid, readily soluble in the common organic solvents.

3.234 mg sub: 7.818 mg CO_2; 3.139 mg H_2O. 6.750 mg sub.: 0.989 ml N_2 (23°, 732 mm). Found %: C 65.97; H 10.86; N 16.28. $C_{14}H_{27}ON_3$. Calculated %: C 66.40; H 10.67; N 16.60.

2-Quinuclidinecarboxylic acid diethylaminoisopentylamide

The acid chloride chlorine hydrate of 2-quinuclidinecarboxylic acid, obtained from 3 g of the acid hydrochloride, was processed in a solution of 4.94 g diethylaminoisopentylamine in 80 ml absolute ether. 3.6 g of a substance with a b.p. of 150-151° at 0.3 mm was obtained (80% of the theoretical). It was a colorless, oily liquid, readily soluble in the common organic solvents.

4.244 mg sub.: 10.635 mg CO_2; 4.217 mg H_2O. 3.990 mg sub.: 9.990 mg CO_2; 4.008 mg H_2O. 4.937 mg sub.: 0.628 ml N_2 (23°, 742 mm). Found %: C 68.38, 68.33; H 11.11, 11.24; N 14.32. $C_{17}H_{33}O_3N_3$. Calculated %: C 68.47; H 11.17; N 14.23.

2-Quinuclidinecarboxylic acid benzylamide

The acid chloride chlorine hydrate of 2-quinuclidinecarboxylic acid obtained from 3 g of the acid hydrochloride was added to a solution of 5.2 g benzylamine in 80 ml absolute ether. The precipitate was filtered and carefully washed in chloroform. The chloroform-and-ether extract was stirred with 50 ml of a 50% potash solution, dried with calcined potash and the solvent driven off. 2.36 g of a substance with a b.p. of 183-185° at 0.2 mm was obtained (62.6% of the theoretical). A colorless, immobile liquid, dissolving readily in the common organic solvents, but with difficulty in water.

3.472 mg sub.: 9.330 mg CO_2; 2.630 mg H_2O. 4.040 mg sub.: 0.425 ml N_2 (29°, 729 mm). Found %: C 73.33; H 8.47; N 11.39. $C_{15}H_{20}ON_2$. Calculated %: C 73.77; H 8.19; N 11.47.

The hydrochloride was a white crystalline substance with m.p. 166-168°, readily soluble in alcohol and water, but insoluble in ether.

14.746 mg sub.: 2.60 ml 0.02 N $AgNO_3$. 14.579 mg sub.: 2.49 ml 0.02 N $AgNO_3$. Found %: Cl 12.50, 12.11. $C_{15}H_{20}ON_2 \cdot HCl$. Calculated %: Cl 12.29.

2-Quinuclidinecarboxylic acid pyridyl-(2')-amide

The acid chloride chlorine hydrate of 2-quinuclidinecarboxylic acid, obtained from 3 g of the acid hydrochloride, was gradually added to a solution of 5.9 g 2-aminopyridine in 50 ml dry pyridine. The reaction mixture was heated for 3 hours at 60-65°. The pyridine was then driven off in vacuum, the residue processed with a 50% potash solution and extracted with ether. The ether extract was dried, the ether driven off, the residue ground with water, and the precipitate thus formed was filtered. It had a weight of 2.2 g (61% of the theoretical) and a melting point of 106-108°. After crystallization out of 33% aqueous alcohol the substance melted at 109-110°. It was soluble in the common organic solvents and insoluble in water. It distilled in vacuum at 149-150° / 0.3 mm.

3.580 mg sub.: 8.938 mg CO_2; 2.527 mg H_2O. 5.058 mg sub.: 0.824 ml N_2 (21.5°, 715 mm). 4.490 mg sub.: 0.771 ml N_2 (25°, 717 mm). Found %: C 68.13; H 7.58; N 17.81, 18.56. $C_{13}H_{17}ON_3$. Calculated %: C 67.53; H 7.35; N 18.18.

N-[Quinuclidinoyl-(2)]-piperidine

The acid chloride chlorine hydrate obtained from 3 g 2-quinuclidinecarboxylic acid hydrochloride, and 4 g piperidine in 50 ml benzene were heated at 60-70° for 12 hours. 1.79 g substance was obtained (51% of the theoretical) with b.p. 129-130° / 0.35 mm, m.p. 72-74°. It was a white crystalline substance soluble both in organic solvents and in water.

4.170 mg sub.: 10.740 mg CO_2; 3.698 mg H_2O. 3.469 mg sub.: 8.917 mg CO_2; 3.071 mg H_2O. 7.198 mg sub.: 0.800 ml N_2 (26°, 729 mm). 7.940 mg sub.: 0.902 ml N_2 (28.5°, 730 mm). Found %: C 70.28, 70.15; H 9.92, 9.91; N 12.17, 12.36. $C_{13}H_{22}ON_2$. Calculated %: C 70.27; H 9.90; N 12.61.

2-Quinuclidinecarboxylic acid thiazolyl-(2')-amide

The acid chloride chlorine hydrate of 2-quinuclidinecarboxylic acid obtained from 3 g of the acid, was added to a solution of 4.7 g 2-amino-thiazole in 50 ml pyridine, and the reaction mixture was heated for 8 hours at 60-70°. Upon cooling, the precipitate deposited was filtered, dissolved in 10 ml water, to which a 50% potash solution was added until an alkaline reaction was obtained with phenolphthalein. The precipitate obtained was filtered, washed with water and recrystallized from the water. It was a white crystalline substance, soluble in organic solvents and in boiling water. The m.p. was 114-116°. The yield was 2.1 g (57% of the theoretical).

3.256 mg sub.: 6.667 mg CO_2; 1.809 mg H_2O. 4.860 mg sub.: 0.796 ml N_2 (25°, 731 mm). Found %: C 55.87; H 6.22; N 18.05. $C_{11}H_{15}ON_3S$. Calculated %: C 56.11; H 6.32; N 17.76.

2-Diethylaminoethylaminomethylquinuclidine

Reduction of 5.07 g 2-quinuclidinecarboxylic acid diethylaminoethylamide by 1.52 g $LiAlH_4$ in 100 ml absolute ether gave 3.2 g of the amine (70% of the theoretical) in the form of a colorless liquid with b.p. 171-173° / 13 mm.

3.105 mg sub.: 7.923 mg CO_2; 3.280 mg H_2O. 3.672 mg sub.: 0.582 ml N_2 (27°, 739 mm). Found %: C 69.63; H 11.84; N 17.53. $C_{14}H_{29}N_3$. Calculated %: C 70.29; H 12.13; N 17.57.

The tripicrate consisted of yellow crystals with an m.p. of 164.5-166.5°.

3.279 mg sub.: 0.549 ml N_2 (28.5°, 727 mm). 4.890 mg sub.: 0.799 ml N_2 (29°, 733 mm). Found %: N 18.15; 17.79. $C_{32}H_{38}O_{21}N_{12}$. Calculated %: N 18.14.

2-Diethylaminoisopentylaminomethylquinuclidine

Reduction of 2.9 g 2-quinuclidinecarboxylic acid diethylaminoisopentylamide by 0.45 g $LiAlH_4$ in 80 ml absolute ether produced 2 g of the amine (72% of the theoretical) in the form of a colorless oily liquid with b.p. 144-146° at 0.2 mm, soluble both in organic solvents and water.

The triphosphate was a white crystalline hygroscopic substance.

4.702 mg sub.: 6.090 mg CO_2; 3.167 mg H_2O. Found %: C 35.35; H 7.54. $C_{17}H_{35}N_3 \cdot 3H_3PO_4$. Calculated %: C 35.47; H 7.65.

2-Benzylaminomethylquinuclidine

4.27 g 2-quinuclidinecarboxylic acid benzylamide was reduced by 1 g $LiAlH_4$ in 100 ml of an ether-benzene mixture (1 : 1). 2.94 g of a substance with b.p. 191° at 0.25 mm was obtained (73% of the theoretical). It was a colorless viscous liquid soluble in organic solvents.

4.380 mg sub.: 0.471 ml N_2 (27°, 739 mm). 4.440 mg sub.: 0.473 ml N_2 (22°, 727 mm). Found %: N 11.89, 11.80. $C_{15}H_{22}N_2$. Calculated %: N 12.17.

The dipicrate consisted of bright yellow crystals with m.p. 190-191°.

5.107 mg sub.: 0.755 ml N_2 (31°, 731 mm). Found %: N 15.95. $C_{27}H_{28}O_{14}N$. Calculated %: N 16.27.

The dihydrochloride was a white crystalline substance with an m.p. of 202-204°.

9.275 mg sub.: 2.99 ml 0.02 N $AgNO_3$. Found %: Cl 23.11. $C_{15}H_{22}N_2 \cdot 2HCl$. Calculated %: Cl 23.43.

2-[Pyridyl-(2')]-aminomethylquinuclidine

4.06 g 2-quinuclidinecarboxylic acid pyridyl-(2')-amide was reduced by 0.8 g $LiAlH_4$ in 200 ml absolute ether. 2.62 g of the amine, having a b.p. of 160° / 0.25 mm was obtained. It was a white crystalline substance readily soluble in organic solvents and in water. M.p. 64-66°.

4.308 mg sub.: 11.363 mg CO_2; 3.325 mg H_2O. 3.323 mg sub.: 8.775 mg CO_2; 2.597 mg H_2O. 3.182 mg sub.: 4.42 ml 0.01 N H_2SO_4. Found %: C 71.98, 72.06; H 8.64, 8.76; N 19.45. $C_{13}H_{19}N_3$. Calculated %: C 71.88; H 8.75; N 19.35.

N-[Quinuclidyl-(2)-methyl]-piperidine

1.75 g N-quinuclidinoyl-(2)-piperidine was reduced by 0.6 g $LiAlH_4$ in 110 ml of absolute ether. 1.24 g of a substance with b.p. 91-93° / 0.2 mm was obtained (75.6% of the theoretical). It was a colorless liquid soluble both in organic solvents and in water.

14.343 mg sub.: 13.23 ml 0.01 N H_2SO_4. Found %: N 12.91. $C_{13}H_{24}N_2$. Calculated %: N 13.12.

The iodomethylate was a white crystalline substance readily soluble in alcohol and water; m.p. 140-142°.

6.111 mg sub.: 10.54 ml 0.01 N $Na_2S_2O_3$. Found %: I 36.50. $C_{14}H_{27}N_2I$. Calculated %: I 36.28.

2-[Thiazolyl-(2)]-aminomethylquinculidine

3.56 g 2-quinuclidinecarboxylic acid thiazolyl-(2')-amide was reduced by 0.7 g $LiAlH_4$ in 120 ml of a benzene-ether mixture (1 : 1). 2.73 g of a substance with b.p. 150-152° / 0.2 mm and m.p. 76-78° was obtained (81% of the theoretical). It was a white crystalline substance readily soluble in alcohol and acetone, poorly soluble in water.

3.716 mg sub.: 8.121 mg CO_2; 2.532 mg H_2O. 5.399 mg sub.: 7.19 ml 0.01 N H_2SO_4. 4.673 mg sub.: 6.19 ml 0.01 N H_2SO_4. Found %: C 59.64; H 7.62; N 18.65, 18.54. $C_{11}H_{17}N_3S$. Calculated %: C 59.19; H 7.62; N 18.83.

2-[6'-Methoxyquinolyl-(4')]-aminomethylquinuclidine

1.8 g 6-methoxy-4-sulfoquinoline, 2.46 g 2-aminomethylquinuclidine and 2.52 ml water were heated with stirring over a Wood bath for 16 hours at 114° (in the reaction mixture). After it had cooled, the reaction mixture was treated with 20 ml water, the white precipitate thus formed was filtered, dissolved in alcohol and then again separated from the alcohol solution by adding water to clouding. The substance obtained had an m.p. of 80-85°. It congealed at 90° and then melted at 140°. After drying the substance in vacuum at 100°, 1.51 g of substance with an m.p. of 143.5-145° was obtained (68% of the theoretical). It consisted of white crystals soluble in alcohol and ether but not in water.

3.848 mg sub.: 10.192 mg CO_2; 2.671 mg H_2O. 6.900 mg sub.: 0.853 ml N_2 (23.5°, 737 mm). Found %: C 72.28; H 7.76; N 13.83. $C_{18}H_{23}ON_3$. Calculated %: C 72.72; H 7.74; N 14.14.

The dihydrochloride was a white crystalline substance with m.p. of 280 - 282°.

7.400 mg sub.: 2.00 ml 0.02 N $AgNO_3$. 14.994 mg sub.: 4.01 ml 0.02 N $AgNO_3$. Found %: Cl 19.07, 18.97. $C_{18}H_{23}ON_3 \cdot 2HCl$. Calculated %: Cl 19.18.

2-Acridyl-(9')-aminomethylquinuclidine

3.3 g 2-aminomethylquinuclidine, 5.4 g 9-phenoxyacridine and 90 ml n-butyl alcohol were heated with boiling for 20 hours. The 1.37 g acridone produced was filtered, and the filtrate evaporated in vacuum. The residue was dissolved in 10% hydrochloric acid, the undissolved portion filtered out, the hydrochloric solution rendered colorless with charcoal and treated with a 15% solution of sodium carbonate until phenolphthalein showed an alkaline reaction. The base thus produced was ground with water in a mortar, and this gave a bright yellow crystalline substance with m.p. 144-146°. The yield was 3.97 g (63% of the theoretical). The substance was soluble in butyl alcohol upon heating, slightly soluble in ether, insoluble in water.

3.701 mg sub.: 10.761 mg CO_2; 2.352 mg H_2O. 3.473 mg sub.: 10.069 mg CO_2; 2.188 mg H_2O. Found %: C 79.35, 79.12; H 7.09, 7.05. $C_{21}H_{23}N_3$. Calculated %: C 79.49; H 7.25.

SUMMARY

A series of 2-alkyl (aryl) aminomethylquinuclidines was synthesized, starting with 2-quinuclidinecarboxylic acid as the initial material.

LITERATURE CITED

[1] M. V. Rubtsov, E. S. Nikitskaya, E. E. Mikhlina, A. D. Yanina and V. Ya. Furshtatova, J. Gen. Chem. 23, 1555 (1953).*

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* See Consultants Bureau English translation, page 1633.

SYNTHESIS OF THIAZOLE DERIVATIVES

X. NITROBENZOTHIAZOLYLCARBINOLS AND THEIR CONVERSION:

V. M. Zubarovsky

A previous communication [1] described a simplified method of synthesizing benzothiazolyl-(2)-carbinol (I) and methyl-[benzothiazolyl-(2)]-carbinol (XIII). These alcohols can now be produced rapidly and in bulk. They may be regarded as readily available benzothiazole derivatives, and it now becomes possible to expand their use as raw materials for the synthesis of new compounds in this series. Certain conversions of these alcohols were effected earlier [2,3]. In the present study we investigated their nitration and the reactions of the nitrogen products thus obtained.

Nitric acid (d 1.52) was used for nitration, while the nitrated mixture was added to solutions of benzothiazolyl-carbinols in concentrated sulfuric acid. Under these conditions, carbinol (I) gave a yield of 79% 6-nitrobenzothiazo-lyl-(2)-carbinol (II). The position of the nitryl in the new compound was demonstrated by its conversion into nitro-benzothiazole-(2)-carboxylic acid (VII), decarboxylation of which gave nitrobenzothiazole (IX), identical with the 6-nitrobenzothiazole described in the literature.

Reduction of carbinol (II) by stannic chloride resulted in the corresponding amino derivative (V).

Oxidation of carbinol (II) gives 6-nitrobenzothiazole-(2)-aldehyde (VI) and 6-nitrobenzothiazole-(2)-carboxy-lic acid (VII); the oxidizing agents used were selenium dioxide in the first instance, and potassium manganate in the second. We were the first to produce the aldehyde (VI) by oxidation of 2-methyl-6-nitrobenzothiazole by selenium dioxide [3]. The method of synthesizing this aldehyde set forth in the present paper must be regarded as more satis-factory than the prior method; while the nitroaldehyde yield continues to be low (30-34%), the method of synthesis is simpler and the product is considerably more pure. The pure aldehyde (VI) has an m.p. of 174°, while previous-ly, despite the most meticulous purification, it was obtained with a 146° m.p. and a somewhat elevated nitrogen con-tent.

The acid (VII) results from oxidation of nitrocarbinol, giving a yield of 70%, and is a colorless microcrystall-ine substance. The nitryl acid is purified by settling hydrochloric acid out of a warm water solution of its sodium salt. When the acid is heated in an open capillary tube it melts at 172-175°, and carbon dioxide is liberated; the acid melts at 174° without noticeable decomposition in a sealed capillary. The acid chloride (X) is obtained from its potassium salt and oxalyl chloride by the method successfully used in the synthesis of the acid chlorides of other heterocyclic acids [4]. The methyl ester (XI) and hydrazide (XII) of the nitro acid were synthesized.

Fridman obtained acid (VII) by nitration of benzothiazole-(2)-carboxylic acid [5], while Mizuno, Adachi and Kanda recently obtained it from 2-trichloromethyl-6-nitrobenzothiazole [6]. Mizuno and associates found the acid (VII) to have an m.p. of 181-182° and do not record decarboxylation accompanying melting.

Fridman describes acid (VII) as a "light yellow amorphous powder, decomposing at 115°", while an effort to obtain its acid chloride and ester did not attain the desired ends. The divergence between our data on the proper-ties of acid (VII) and those of Fridman caused us to undertake the nitration of benzothiazole-(2)-carboxylic acid (VIII). For this purpose we introduced a new method — oxidation of carbinol (I) by potassium permanganate. This method is simple, quick, and produces a very pure product. The methods of producing this acid described in the lit-erature [7,8,9] are more complicated. We take this opportunity to state that the acid chloride (VIII) is readily ob-tained from oxalyl chloride and the potassium salt of the acid; the acid chloride thus synthesized has a melting point of 116-118°, while the literature describes it as 100° [10] and 102° [11].

Nitration of acid (VIII) produces a yellow acid, difficult to free of contaminants (VII). Crystallization of the product by decarboxylation of this acid results in a small quantity of pure 6-nitrobenzothiazole, while concentra-tion of the mother liquor is accompanied by liberation of a product with a low boiling point (an isomer mixture, per-haps ?).

Thus, nitration of acid (VIII) as a method of synthesizing acid (VII) is not deserving of attention.

Nitration of methyl-[benzothiazolyl-(2)]-carbinol (XIII) was conducted in a manner analogous to nitration of carbinol (I).
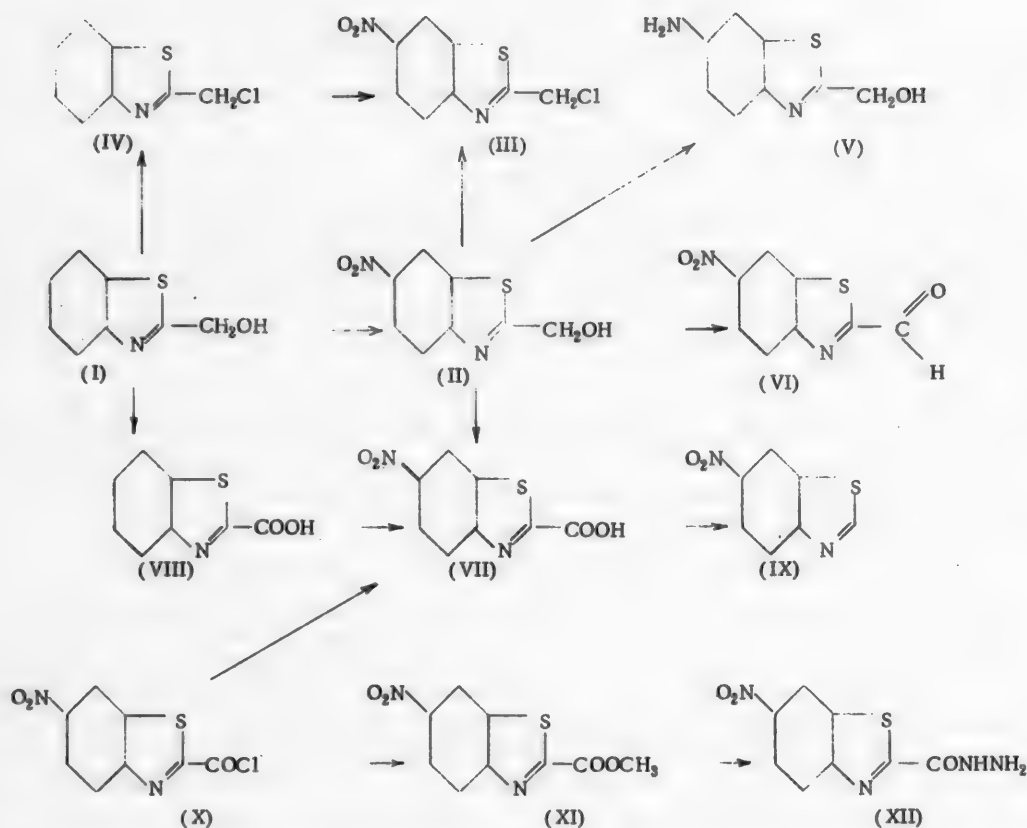
The nitration product, methyl-[6-nitrobenzothiazolyl-(2)]-carbinol (XIV) was subjected to the same conversions as its analog — carbinol (II).

These conversions gave: the oxidation product, methyl-[6-nitrobenzothiazolyl-(2)]-ketone (XVII), the reduction product, methyl-[6-amino-benzothiazolyl-(2)]-carbinol (XVIII) and the chlorine-for-alcohol-group substitution product — 6-nitro-2-(a -chloroethyl)-benzothiazole (XV). The latter also results from the nitration of 2-(a -chloroethyl)-benzothiazole (XVI).
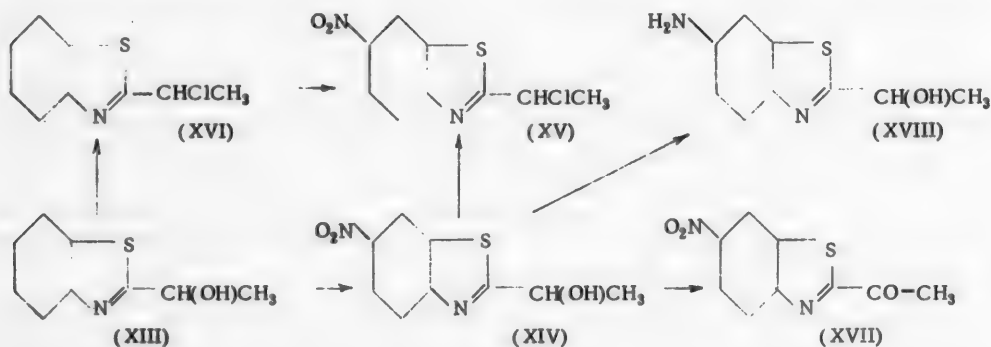
The ketone (XVII) was oxidized by potassium permanganate into the acid (VII), from which 6-nitrobenzothiazole (IX) was obtained, this being the means by which the structure of all the nitro and amino derivatives synthesized from carbinol (XIII) was determined.

EXPERIMENTAL

1. 6-Nitrobenzothiazolyl-(2)-carbinol (II). Benzothiazolyl-(2)-carbinol, twice recrystallized from toluol, was chosen for nitration. The carbinol (24.75 g; 0.15 mole) was dissolved in 20 ml concentrated sulfuric acid. To accomplish this, carbinol was added, bit by bit, to sulfuric acid in a porcelain mortar, and after each addition, the mixture was ground until the formation of a solution in which a cloudy appearance was not objectionable, but in which a noticeable yellow color was impermissible as this was a sign that the carbinol was not pure enough.

The thick, viscous solution was transferred to a reaction vessel with stirrer, thermometer and dropping funnel, where it was nitrated with a mixture consisting of 14.25 g (9.4 ml; 0.225 mole) nitric acid (d 1.52) and 15 ml concentrated sulfuric acid. The reaction vessel was placed in a bath containing a coolant mixture, and the nitrating mixture was added over a period of 30 minutes at a temperature (in the reaction mixture) not exceeding 10°. When the addition was completed, the ice bath was removed and stirring continued until the temperature rise due to exothermic reaction ceased. The reaction vessel was then placed in a warm water bath and a 60° temperature was maintained within the reaction vessel for an hour and a half, upon which heating was brought to an end and the mixture set aside for 15 hours. The mixture was then poured into 400 ml of water containing pieces of ice, the yellow-white precipitate filtered off, washed by suspension with 100 ml of a 10% aqueous sodium carbonate solution, 100 ml of a 10% hydrochloric acid solution, and water. The yield of dry nitro product was 25 g (79.3% of the theoretical).

After crystallization from 80 ml ethyl alcohol (1 g per 4 ml, charcoal being used), 14 g nitrocarbinol in the form of thin yellow white needles with a melting point of 153° was obtained. The colorless nitrocarbinol was obtained upon recrystallization from a mixture of water and acetone (1 : 1) and then had an m.p. of 165°.[*]

Found %: S 15.52, 15.58. $C_8H_6O_3N_2S$. Calculated %: S 15.24.

2. 2-Chloromethyl-benzothiazole (IV). 4.95 g (0.03 mole) benzothiazolyl-(2)-carbinol and 6.9 g (0.033 mole) phosphorous pentachloride, both pulverized, were rapidly mixed in a round-bottomed flask, which was immediately connected to a reflux condenser and placed in a coolant mixture of ice and salt. An exothermic reaction soon began, and a semi-solid brown mass was formed which was heated for 10 minutes in boiling water upon the conclusion of the exothermic reaction. Ice and then a 20% aqueous solution of sodium carbonate were added to the cooling mass until an alkaline reaction was obtained. Lumps were carefully crushed and the oily brown product extracted with ether. The extract was dried with calcium chloride, the solvent driven off and the residue vacuum-distilled. A fraction with a b.p. of 110° / 2 mm was collected. The yield was 3.0 g (54.5% of the theoretical). It was a colorless oil, crystallizing as it cooled. The chloride was recrystallized from petroleum ether (the solution was shaken up with charcoal, concentrated and cooled with ice) and obtained in the form of colorless crystals with an m.p. of 34°.

Found %: N 7.55, 7.58. C_8H_6NSCl. Calculated %: N 7.63.

3. 6-Nitro-2-chloromethyl-benzothiazole (III). A. From 6-nitrobenzothiazolyl-(2)-carbinol. 3.15 g (0.015 mole) 6-nitrobenzothiazolyl-(2)-carbinol and 3.12 g (0.015 mole) phosphorous pentachloride were used in this synthesis. The method did not differ in any respect from that of the preceding experiment, No. 2. Addition of the sodium carbonate solution produced a precipitate, which was filtered out, washed with water, desiccated and recrystallized (carbon) from ligroin (with a b.p. of 100-120°). The yield of substance, once recrystallized, was 1.5 g (43% of the theoretical); the product consisted of colorless crystals with an m.p. of 101°. Recrystallization from ligroin gave 6-nitro-2-chloromethylbenzothiazole with an m.p. of 105°.

Found %: N 11.95, 12.15. $C_8H_5O_2N_2SCl$. Calculated %: N 12.26.

B. From 2-chloromethyl-benzothiazole. 1.84 g (0.01 mole) of 2-chloromethyl-benzothiazole was dissolved in 2 ml concentrated sulfuric acid and nitrated with a mixture of 0.95 g (0.015 mole) nitric at 1.52 and 1 ml concentrated sulfuric acid. The conditions of nitration were described above under Experiment 1. The nitrated mixture was poured onto ice; the viscous substance resulting soon solidified. It was washed in a sodium carbonate solution and in water, and recrystallized from 30 ml ligroin (charcoal used).

The yield of recrystallized substance was 1.0 g (43.5% of the theoretical). 6-Nitro-2-chloromethyl-benzothiazole twice recrystallized from ligroin had an m.p. of 103°, and a mixture thereof with the same compound, obtained by method A, melted at 103-104°.

4. 6-Aminobenzothiazolyl-(2)-carbinol (V). 2.1 g (0.01 mole) 6-nitrobenzothiazolyl-(2)-carbinol was added, bit by bit, with stirring, to 7.3 g (0.033 mole) stannic chloride dissolved in 8.2 ml concentrated hydrochloric acid, heated to 75°. Each addition resulted in the appearance of an orange coloration which disappeared with stirring. The mixture was heated for an hour in a boiling water bath and left for 12 hours, upon which ice and a 20% solution of

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[*] Corrected melting and boiling temperatures are used throughout for the substances undergoing analysis.

caustic soda were added until the white stannic hydroxide precipitate disappeared. The yellow crystalline aminobenzothiazolyl carbinol precipitate was filtered out and repeatedly washed in a 2% aqueous sodium hydroxide solution. The yield of aminocarbinol was 1.0 g (55% of the theoretical). After single distillation from xylol (with use of charcoal), the aminocarbinol was obtained in the form of small yellow-white crystals with an m.p. of 151°. 6-Aminobenzothiazolyl-(2)-carbinol is readily soluble without heating in dilute hydrochloric acid (1 : 5), ethyl alcohol and dioxan; it can be diazotized, and its diazocompounds combine with β -naphthol to form an orange-yellow dye.

Found %: N 15.91; S 17.62, 17.45. $C_8H_8ON_2S$. Calculated %: N 15.56; S 17.77.

5. 6-Nitrobenzothiazole-(2)-aldehyde (VI). A warm solution of 6.65 g (0.06 mole) selenium dioxide in 30 ml dioxan and 3 ml water was added suddenly to 10.5 g (0.05 mole) 6-nitrobenzothiazolyl-(2)-carbinol. The mixture was heated with uninterrupted mixing to rapid boiling, and boiled two hours. The selenium precipitate was filtered off and the filtrate poured into 250 ml water. The yellow product liberated was filtered*, washed in water and, while moist, twice crystallized from an acetone-water mixture (5 : 4), while the portion that failed to dissolve in hot aqueous acetone was discarded. The mother liquors were decolorized with a considerable amount of charcoal, and were cooled for a long period with ice. The nitroaldehyde yield was 3.5 g (33.6% of the theoretical) the m.p. 169°. After two further crystallizations from ethyl alcohol (10% charcoal) the aldehyde was obtained as colorless, odorless crystals with m.p. 174°.

Found %: N 13.38, 13.40. $C_8H_4O_3N_2S$. Calculated %: N 13.46.

The nitroaldehyde thiosemicarbazone, recrystallized from glycol, had a decomposition temperature of 287-289°. It was also prepared by oxidizing 6-nitro-2-methyl-benzothiazole [3]; after crystallization from glycol its decomposition temperature was 287°, and a mixture of the two thiosemicarbazone samples decomposed at 287° when heated in a capillary tube.

6. 6-Nitrobenzothiazole-(2)-carboxylic acid (VII). This synthesis was performed on the basis of 6-nitrobenzothiazolyl-(2)-carbinol, twice recrystallized, once from ethyl alcohol and once from aqueous acetone. 10.5 g (0.05 mole) of this compound was introduced into 2 liters of hot water, and the suspension heated to active boiling, at which point a yellow solution was formed. Heating was suspended, and when the temperature dropped to 90°, a warm solution of 7.9 g (0.05 mole) potassium permanganate in 500 ml water was added. Mixing continued, and within 7 minutes the manganese dioxide precipitate was filtered off and washed in a small quantity of boiling water. 10 ml concentrated hydrochloric acid was added to the warm filtrate, with stirring, and the white precipitate was filtered, washed in water and air dried. The nitro acid yield was 7.85 g (70% of the theoretical).

The acid was converted to a sodium salt, and the latter precipitated out of a warm aqueous solution by hydrochloric acid. After air drying the acid had a b.p. of 165-171°, at which decomposition occurred. When the acid was heat dried, partial decarboxylation occurred, and analysis showed an elevated nitrogen content. Air and desiccator drying, however, went slowly. The sodium salt of the acid, obtained by dissolving the acid in a warm water solution of sodium carbonate with subsequent cooling of the solution obtained, was subjected to analysis. The salt was twice recrystallized out of water (the mother liquors having been shaken with charcoal) and obtained in the form of colorless crystals with a pearl-like luster, having a decomposition temperature of 335°. The salt contained water of crystallization, readily discovered in the usual manner, which was lost uponupon vacuum drying at 135°. Prior to the drying of the salt:

Found %: N 10.54, 10.53. $C_8H_3O_4N_2SNa \cdot H_2O$. Calculated %: N 10.60.

After drying:

Found %: N 11.26. $C_8H_3O_4N_2SNa$. Calculated %: N 11.38.

The nitro acid, isolated from the pure twice recrystallized sodium salt, washed in alcohol and ether, and dried in a vacuum desiccator, melted in an open capillary at 172-175° with liberation of carbon dioxide, and in a closed capillary at 174° without noticeable decomposition.

To obtain the potassium salt of the acid, 2.4 g (0.0175 mole) of potassium carbonate was dissolved in 60 ml water, and 7.85 g (0.035 mole) 6-nitrobenzothiazole-(2)-carboxylic acid was added, bit by bit, with stirring, to the solution, heated to 70-75°. During the addition it was necessary to make sure that the potassium salt did not crystallize, and to heat the solution when a precipitate appeared. The precipitate was shaken with charcoal, filtered and ice cooled. The crystallized salt was filtered, ground with alcohol in a mortar, again filtered, washed in alcohol until

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* In repetitions of the experiment, filtration of this precipitate sometimes proved difficult; when this occurred it was necessary to add a few milliliters of a saturated sodium chloride solution to the suspension.

a colorless filtrate appeared, and then in ether. The yield was 7 g, and the decomposition temperature, 268°.

7. Decarboxylation of 6-nitrobenzothiazole-(2)-carboxylic acid. 0.9 g 6-nitrobenzothiazole-(2)-carboxylic acid was heated in a test tube in an air bath until liberation of carbon dioxide ceased. The test tube residue, which solidified upon cooling, was recrystallized (with the aid of charcoal) from ethyl alcohol. After being cooled with ice, the pale-yellow crystalline precipitate (IX) was filtered, and weighed after drying 0.6 g (85.7% of the theoretical); the m.p. was 174°. The m.p. of a mixture of this decarboxylation product (1:1) with known 6-nitrobenzothiazole (m.p. 173-174° [12]) was 174°.

8. 6-Nitrobenzothiazole-(2)-carboxylic acid chloride. (X). The potassium salt of 6-nitrobenzothiazole-(2)-carboxylic acid was dried for 3 hours at 110-130°, and then in a vacuum desiccator over sulfuric acid. A solution of 3.2 g (0.025 mole) oxalyl chloride in 10 ml dry benzene was added, drop by drop, with stirring, to an ice-cooled suspension of 6.55 g (0.025 mole) fine powder of the salt in 25 ml dry benzene. The addition was performed at a rate that prevented noticeable evolution of heat by the mixture, and, in any case, so that its temperature would not exceed 10°. When addition was completed, mixing continued for another 15 minutes, upon which the bath containing ice was replaced by a cold water bath, whereupon the latter, after half an hour, was slowly warmed to the point at which, after 25-30 minutes, it reached the boiling point; it was then kept boiling for another 30 minutes. The hot contents of the reaction vessel were filtered, the filtrate cooled in ice for an hour, the orange acid chloride precipitate filtered and washed with petroleum ether. The yield was 2.5 g (31%). The acid chloride was heated with 30 ml dry benzene, the insoluble portion discarded, and the solution, after shaking with charcoal and filtration, was concentrated and cooled. The pure acid chloride was a pale-yellow fine crystalline powder with an m.p. of 138°.

Found %: N 11.39. $C_8H_3O_3N_2SCl$. Calculated %: N 11.55.

The acid chloride reacts violently with ammonia in aqueous solution, forming 6-nitrobenzothiazole-(2)-carboxylic acid amide, consisting of colorless fine crystals with an m.p. of 280° (butyl alcohol).

9. 6-Nitrobenzothiazole-(2)-carboxylic acid methyl ester (XI). A mixture of 2.0 g 6-nitrobenzothiazole-(2)-carboxylic acid chloride and 30 ml anhydrous methyl alcohol was boiled for two hours and then set aside for 15 hours. The precipitate was filtered and recrystallized from methyl alcohol (with the aid of charcoal). The yield was 1.0 g (51% of the theoretical); m.p. 178°. After double crystallization with charcoal from a mixture (12 ml mixture to 1 g ether) of dioxan and ethyl alcohol (1 : 2), the 6-nitrobenzothiazole-(2)-carboxylic acid methyl ester appeared in the form of fine colorless needles, m.p. 179°.

Found %: N 11.97. $C_9H_6O_4N_2S$. Calculated %: N 11.76.

6-Nitrobenzothiazole-(2)-carboxylic acid ethyl ester is obtained similarly to the production of the ethyl alcohol acid chloride. It consists of colorless needles with m.p. 182° (from ethyl alcohol).

10. 6-Nitrobenzothiazole-(2)-carboxylic acid hydrazide (XII). 1.95 g (0.04 mole) of hydrazine hydrate dissolved in 6 ml alcohol was added, with stirring, to 1.2 g (0.005 mole) 6-nitrobenzothiazole-(2)-carboxylic acid methyl ester suspended in 15 ml ethyl alcohol. The mixture was heated for half an hour in boiling water, whereupon it was cooled in ice, and the bright, fine crystalline precipitate was filtered and washed on the filter with alcohol diluted with water (1 : 1) until the draining filtrate was no more than faintly yellow; the precipitate was then washed with alcohol and ether. Yield 0.9 g (75%). The hydrazide was purified by crystallization from an ample mixture of ethyl alcohol and water (3 : 2), and the solution was decolorized with alcohol. Slow cooling was accompanied by the appearance of fine light-yellow needles, which were filtered off and washed in alcohol and ether. The hydrazide melted, with decomposition, at 215-217°.

Found %: N 23.38, 23.70. $C_8H_6O_3N_4S$. Calculated %: N 23.53.

11. Benzothiazole-(2)-carboxylic acid (VIII). Benzothiazole-(2)-carbinol, recrystallized from toluol, was used. 33 g (0.2 mole) benzothiazole-(2)-carbinol, pulverized, was added, with stirring, to 2 liters water, heated to 80°; the solution was quickly filtered. 31.6 g (0.2 mole) potassium permanganate in 250 ml hot water was added (in 5 to 10 min), with stirring, to the hot filtrate (75°). Without further heating, stirring was continued for another 5 minutes, the MnO_2 filtered off, and the acid extracted with a small quantity of boiling water. The filtrate was allowed to cool to 35°, then 40 ml concentrated HCl was added all at once. The suspension was cooled by ice, and the fine, white crystalline benzothiazole-(2)-carboxylic acid precipitate was filtered and washed on the filter with cold water, then with ether. 22 g acid (61% of the theoretical); m.p. 106-108°, (decomp.) (literature data m.p. 108°, with decomp. [7]). The acid potassium salt resulted from equivalent amounts of the acid and potash. 26.85 g (0.15 mole) of the acid was added to warm solution of 10.35 g (0.075 mole) potash in 185 ml water, the mixture was heated to complete solution of the precipitate, the solution allowed to cool and then cooled with ice. Crystallized salt was filtered off and washed with ether. Yield 21.8 g, m.p. 370° (decomp.). Evaporation of the mother liquor over a water bath provided additional quantities of the salt.

Benzothiazole-(2)-carboxylic acid chloride was obtained in the same manner as 6-nitrobenzothiazole-(2)-carboxylic acid chloride (experiment No. 8). The benzothiazole-(2)-carboxylic acid potassium salt was dried at 125° and then in a vacuum desiccator over sulfuric acid. After the acid chloride was filtered out of the cooled benzene solution, the bulk of the solvent was distilled off the filtrate and more of the acid chloride was obtained from the concentrate. 5.0 g (63.2%) acid chloride was obtained from 8.7 g (0.04 mole) benzothiazole-(2)-carboxylic acid potassium salt and 5.0 g (0.04 mole) oxalyl chloride. The crude acid chloride, comprising pale yellow needles, had an m.p. of 115°. After double crystallization (with charcoal) from petroleum ether, the acid chloride was obtained in the form of yellow-white crystals, m.p. 116-118°.

Found %: N 7.15, 7.12. C_9H_4ONSCl. Calculated %: N 7.09.

12. Nitration of benzothiazole-(2)-carboxylic acid. 5.9 g (0.033 mole) benzothiazole-(2)-carboxylic acid was dissolved in 10 ml concentrated sulfuric acid, and the thick yellow solution thus formed was nitrated with a mixture consisting of 3.15 g (0.05 mole) nitric acid (d 1.52) and 3.5 ml concentrated sulfuric acid. The method of nitration was the same as that used in Experiment No. 1 for the synthesis of 6-nitrobenzothiazole-(2)-carbinol. After the nitrated mixture had been poured into 150 ml water containing ice, the yellow precipitate was filtered, washed in water and heated (50°) when moist with a solution of 3.0 g potash in 75 ml water. The solution was partially decolorized by charcoal and acidified with hydrochloric acid. The nitro acid thus evolved was filtered, washed with water and air dried. The yield was 5.5 g, m.p. 115-117°.

1.0 g nitro acid was subjected to decarboxylation. The product thus formed was crystallized from 14 ml ethyl alcohol (with use of charcoal). 0.3 g 6-nitrobenzothiazole, m.p. 175°, was obtained. A yellow crystalline powder with m.p. 115° separated out of the mother liquor, and when crystallized from alcohol the product had an m.p. of 127°

13. Methyl-[6-nitrobenzothiazolyl-(2)-]-carbinol (XIV). The colorless carbinol obtained after double distillation of the raw carbinol from toluol (1 ml solvent to 2 g carbinol) or from a mixture of toluol (1 volume) and ligroin (1.5 volume) was used for purposes of nitration. In the latter case 3.5 ml mixture was needed for each gram carbinol. Whichever type of crystallization was used, the mother liquors were decolorized with charcoal and then cooled in ice. The nitration of methyl-[benzothiazolyl-(2)-] carbinol proceeded in a manner entirely analogous to that of benzothiazolyl-(2)-carbinol (Experiment 1). Ingredients in the following quantities were employed in the experiments: 17.9 g (0.1 mole) methyl-[benzothiazolyl-(2)]-carbinol, and 16 ml concentrated sulfuric acid to dissolve it; the nitrated mixture consisted of 9.5 g (6.25 ml; 0.15 mole) nitric acid (d 1.52) and 10 ml concentrated sulfuric acid. The product was filtered an hour after the nitrated mixture was poured into the water. The nitro product yield was 15 g (67% of the theoretical). The raw nitro product was crystallized from 85 ml ethyl alcohol (with use of charcoal). After a single crystallization the methyl-[6-nitrobenzothiazolyl-(2)]-carbinol had an m.p. of 172°. For purposes of analysis it was twice more recrystallized from ethyl alcohol and obtained as small yellow-white crystals, m.p. 176°.

Found %: N 12.57, 12.65. $C_9H_8O_3N_2S$. Calculated %: N 12.50.

14. 2-(a -Chloroethyl)-benzothiazole (XVI). The synthesis of this chloride was analogous to the synthesis of 2-chloromethyl-benzothiazole (Experiment 2). 7.15 g (0.04 mole) methyl-[benzothiazolyl-(2)-]-carbinol and 9.15 g (0.044 mole) phosphorous pentachloride were reacted. After mixing the reaction product with ice, a 20% excess of aqueous sodium hydroxide solution was added (30 ml), and the semi-solid oily chunks were carefully crushed. Fourfold ether extraction was required. Upon distillation of the raw product a fraction was obtained that boiled between 112 and 117°/3-4 mm. The yield was 5.0 g (63.2% of the theoretical). Upon redistillation the chloride boiled at 115-116°/4 mm. It was a colorless liquid with a characteristic odor, which darkened and took on a greenish fluorescence with the passage of time.

Found %: N 6.72, 6.80. C_9H_8NSCl. Calculated %: N 7.09.

15. 6-Nitro-2-(a -chloroethyl)-benzothiazole (XV). A. From methyl-[6-nitrobenzothiazolyl-(2)]-carbinol . 2.25 g (0.01 mole) methyl-[6-nitrobenzothiazolyl-(2)]-carbinol and 2.3 g (0.011 mole) phosphorous pentachloride were used. The method used was that of Experiment 3, variant A. After grinding with a sodium carbonate solution, the raw chloride was filtered, washed in water and recrystallized from ligroin (b.p. 100-120°; charcoal was used). The mother liquor was cooled with ice. Yield after one crystallization was 1.25 g (50%); m.p. 105°. When twice recrystallized, the chloride consisted of colorless crystals, m.p. 112°.

Found %: N 11.72, 11.54. $C_9H_7O_2N_2SCl$. Calculated %: N 11.55.

B. From 2-(a -chloroethyl)-benzothiazole. 1.98 g (0.01 mole) 2-(a -chloroethyl)-benzothiazole, dissolved in 2 ml concentrated sulfuric acid, was nitrated as in Experiment 3, variant B. The nitration mixture consisted of 0.95 g

(0.015 mole) nitric acid (d 1.52) and 1 ml concentrated sulfuric acid. The nitro product was crystallized out of ligroin. Yield 1.2 g (50% of the theoretical). The nitro product m.p. was 112°, and a mixture thereof with the product obtained by the previous variant, A, of the present experiment, melted at 112°.

16. Methyl-[6-aminobenzothiazolyl-(2)]-carbinol (XVIII). Reduction of methyl-[6-nitrobenzothiazolyl--(2)]-carbinol followed exactly the same lines as reduction of 6-nitrobenzothiazolyl-(2)-carbinol in Experiment 4. The ingredients and their quantities were: 3.36 g (0.015 mole) stannous chloride and 12.5 ml concentrated hydrochloric acid. 60 ml 20% aqueous sodium hydroxide solution was required to separate the synthesized aminocarbinol from the acid solution. The aminocarbinol yield was 2.4 g (82.4%). The product was purified by crystallization from ample xylol (charcoal was used) and was washed in petroleum ether. Methyl-[6-aminobenzothiazolyl-(2)-carbinol was obtained as transparent and virtually colorless needles, m.p. 220°. The aminocarbinol was readily soluble without heating in dilute (1 : 5) hydrochloric acid, and combined to form a diazo compound, which, with β - naphthol, gave an orange-red dye as product.

Found %: N 14.33, 14.34. $C_9H_{10}ON_2S$. Calculated %: N 14.43.

17. Methyl-[6-nitrobenzothiazolyl-(2)]-ketone. (XVII). This ketone was obtained by oxidizing methyl-[6-nitrobenzothiazolyl-(2)]-carbinol with chromium trioxide in an acetic acid medium in a manner similar to the synthesis of methyl-benzothiazolyl-(2)-ketone previously proposed by us [2].

2.6 g (0.026 mole) chromium trioxide in 10 ml glacial acetic acid and 3 ml water was added through a dropping funnel to a hot solution (110°) of 6.7 g (0.03 mole) methyl-[6-nitrobenzothiazolyl-(2)]-carbinol in 25 ml glacial acetic acid at such a rate as to cause the liquid to boil moderately at its surface. This addition took only a few minutes. The mixture was then boiled for 5 minutes and stirred for another 10 minutes without heating. When cooled, the mixture was diluted with 50 ml water, and the precipitate thus formed was filtered and washed in 20% aqueous acetic acid until the wash liquid became colorless. The ketone yield was 5.6 g (84% of the theoretical). The ketone was recrystallized in its entirety from a 100 ml mixture of dioxan (1 volume) and ethyl alcohol (2 volumes), the mother liquors being decolorized with ample charcoal. The product consisted of yellowish needles, m.p. 188°. For purposes of analysis, the ketone was recrystallized twice more, the first time from ethyl alcohol, and the second from the mixture described above, the product being pale-yellow needles, m.p. 191°.

Found %: N 12.74, 12.58. $C_9H_6O_3N_2S$. Calculated %: N 12.61.

Unlike methyl-benzothiazolyl-(2)-ketone, having a strong, pleasant aroma, the present ketone had no odor. The thiosemicarbazone ketone, prepared in the usual manner (with an 83% yield), consisted, after double crystallization from ample isobutyl alcohol, of small yellow crystals with a marked decomposition temperature of 272°.

18. Oxidation of methyl-[6-nitrobenzothiazolyl-(2)]-ketone. 0.75 g potassium permanganate dissolved in 20 ml water was poured into a hot suspension of 0.3 g methyl-[6-nitrobenzothiazolyl-(2)]-ketone in 40 ml water. The mixture was boiled for 10 minutes and the manganese dioxide precipitate was filtered off. 1 ml hydrochloric acid was added to the warm yellow filtrate, and the 6-nitrobenzothiazole-(2)-carboxylic acid thus precipitated was filtered off after half an hour, washed with water and air dried. 0.2 g nitro acid was obtained, and decarboxylated by careful heating in a test tube. The decarboxylation product was recrystallized from 8 ml ethyl alcohol (with charcoal), and 0.1 g of virtually colorless 6-nitrobenzothiazole crystals, melting at 175°, was obtained; when mixed with 6-nitrobenzothiazole of known composition (m.p. 174°), it melted at 174°.

SUMMARY

1. Nitration of benzothiazole-(2)-carbinol and methyl-[benzothiazolyl-(2)]-carbinol, dissolved in concentrated sulfuric acid, by nitric acid (d 1.52), produced satisfactory yields of the 6-nitro derivatives of these alcohols. Certain conversions of nitrobenzothiazolylcarbinols were studied, and some new 6-nitro- and 6-amino-substituted benzothiazole series compounds were obtained, as well as 2-chloromethyl and 2-(α -chloroethyl)-benzothiazoles.

2. An improved method of producing 6-nitrobenzothiazolyl-(2)-aldehyde, and convenient methods of synthesizing methyl-[6-nitrobenzothiazolyl-(2)]-ketone, benzothiazole-(2)- and 6-nitrobenzothiazole-(2)-carboxylic acids were proposed.

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SYNTHESIS OF NITRO, AMINO, AND HYDROXY DERIVATIVES
IN THE DIPHENYLETHANE SERIES

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The p,p'-dihydroxy derivatives of diphenylethane (IV) are known [1] to include such most physiologically active compounds as meso-p,p'-dihydroxy-2,3-diphenylbutane (IV, R = CH_3), meso-p,p'-dihydroxy-3,4-diphenylhexane (IV, R = C_2H_5), meso-p,p'-dihydroxy-4,5-diphenyloctane (IV, R = C_3H_7) and others of marked estrogenic effect.

Moreover, compounds having high curare-like activity [2] have been found among the p,p'-diammonium derivatives of the diphenylethanes.

In this connection, a series of p,p'-diamino derivatives of diphenylethane were synthesized and converted, on the one hand, into p,p'-dihydroxy derivatives and, on the other, into p,p'-diammonium derivatives.

The present paper describes the synthesis of hydrocarbons of the diphenylethane series (I) and their conversion into p,p'-dinitro (II), p,p'-diamino (III) and p,p'-dihydroxy derivatives (IV).

$$C_6H_5-CH-CH-C_6H_5 \rightarrow O_2NC_6H_4-CH-CH-C_6H_4NO_2 \rightarrow$$
$$\qquad\quad | \quad\ | \qquad\qquad\qquad\qquad | \quad\ |$$
$$\qquad\quad R \quad R \qquad\qquad\qquad\qquad\quad R \quad R$$
$$\qquad\qquad (I) \qquad\qquad\qquad\qquad\qquad\qquad (II)$$

$$\rightarrow H_2NC_6H_4-CH-CH-C_6H_4NH_2 \rightarrow HOC_6H_4-CH-CH-C_6H_4OH$$
$$\qquad\qquad\qquad | \quad\ | \qquad\qquad\qquad\qquad\quad | \quad\ |$$
$$\qquad\qquad\qquad R \quad R \qquad\qquad\qquad\qquad\quad R \quad R$$
$$\qquad\qquad\qquad (III) \qquad\qquad\qquad\qquad\qquad (IV)$$

$$(R = H, CH_3, C_2H_5, C_3H_7 \text{ and } C_4H_9).$$
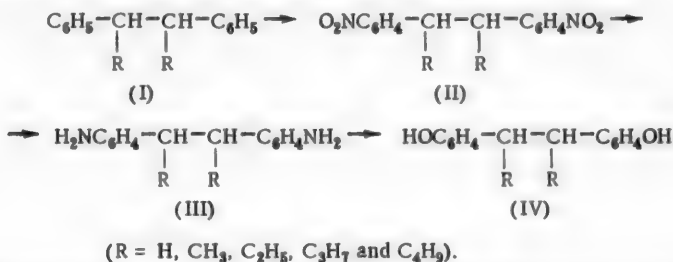
Further, tetranitro (VI) and tetraamino derivatives (VII) were obtained from meso-3,4-diphenylhexane (V).

$$C_6H_5-CH-CH-C_6H_5 \rightarrow (O_2N)_2C_6H_3-CH-CH-C_6H_3(NO_2)_2 \rightarrow$$
$$\qquad\quad | \quad\ | \qquad\qquad\qquad\qquad\quad | \quad\ |$$
$$\qquad\quad R \quad R \qquad\qquad\qquad\qquad\qquad R \quad R$$
$$\qquad\qquad (V) \qquad\qquad\qquad\qquad\qquad\qquad (VI)$$

$$\rightarrow (H_2N)_2C_6H_3-CH-CH-C_6H_3(NH_2)_2$$
$$\qquad\qquad\qquad\quad | \quad\ |$$
$$\qquad\qquad\qquad\quad R \quad R$$
$$\qquad\qquad\qquad\qquad (VII)$$

$$(R = C_2H_5).$$
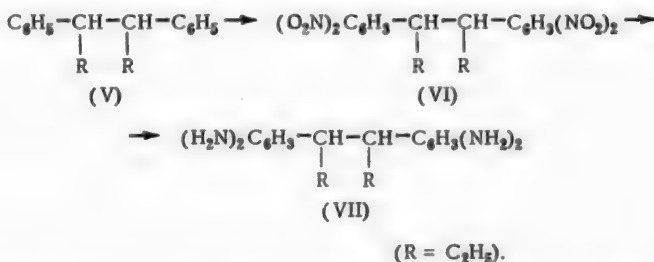
The simplest system for obtaining these hydrocarbons is undoubtedly the following:

$$X-CH-CH-X + 2C_6H_6 \rightarrow C_6H_5-CH-CH-C_6H_5 + 2HX$$
$$\quad | \quad\ | \qquad\qquad\qquad\qquad\quad | \quad\ |$$
$$\quad R \quad R \qquad\qquad\qquad\qquad\quad R \quad R$$
$$\quad (VIII) \qquad\qquad\qquad\qquad\qquad (I)$$

$$(R = \text{hydrogen or alkyl; } X = \text{halide}).$$
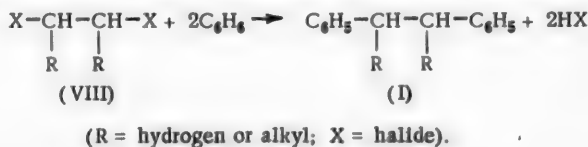
However, this method is convenient only when the required dihalide derivatives are available.

The synthesis of diphenylethane (I, R = H) by this method has been described [3,4] and was repeated by us. We also used this method, starting with 2,3-dibromobutane [5], to synthesize 2,3-diphenylbutane (I, R = CH_3) [6,7] although the yield of meso-forms of this compound was not large.

To obtain 3,4-diphenylhexane (I, R = C_2H_5) [8], 4,5-diphenyloctane (I, R = C_3H_7) [9] and 5,6-diphenyldecane (I, R = C_4H_9) [9,10], described in the literature, the following system was used:

$$C_6H_5-\underset{R}{\underset{|}{CHOH}} \rightarrow C_6H_5-\underset{R}{\underset{|}{CHX}} \rightarrow C_6H_5-\underset{R}{\underset{|}{CH}}-\underset{R}{\underset{|}{CH}}-C_6H_5$$

(IX)   (X)   (I)
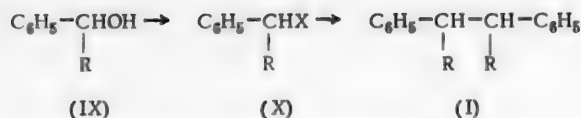
($R = C_2H_5$, C_3H_7 or C_4H_9; X = chlorine).

The carbinols, specifically ethylphenylcarbinol (IX, $R = C_2H_5$) [8,10], propylphenylcarbinol (IX, $R = C_3H_7$) [11] and butylphenylcarbinol (IX, $R = C_4H_9$) [11] have been described. We produced them by the Grignard reaction from the corresponding alkyl haloid (ethyl bromide, propyl chloride or butyl bromide) and benzaldehyde.

Conversion of the carbinols into the homologous chlorides — 1-phenyl-1-chloropropane (X, $R = C_2H_5$), 1-phenyl-1-chlorobutane (X, $R = C_3H_7$) and 1-phenyl-1-chloropentane (X, $R = C_4H_9$), was performed by the method described in the literature [12] of reacting the carbinols with thionyl chloride. 1-Phenyl-1-chloropropane was also obtained by saturating phenylethylcarbinol with hydrogen chloride [13,14]. Phosphorous trichloride was used in this instance to cause completion of the reaction. The addition of this last compound to the saturation product took place after removal of the layer of water formed during the saturation process.

3,4-Diphenylhexane (I, $R = C_2H_5$), 4,5-diphenyloctane (I, $R = C_3H_7$) and 5,6-diphenyldecane (I, $R = C_4H_9$), are known to be able to be derived from the corresponding halo derivatives when the latter are reacted with sodium [8,9], magnesium [10] or iron [14], although the hydrocarbon yield is not high. We found that of these three metals, magnesium gives the best results in reaction with 1-phenyl-1-chloropropane (X, $R = C_2H_5$), and we also used it in reaction with 1-phenyl-1-chlorobutane (X, $R = C_3H_7$) and 1-phenyl-1-chloropentane (X, $R = C_4H_9$).

It must be noted that all the hydrocarbons we synthesized, except diphenylethane, contained two assymetrical carbon atoms, so that their synthesis resulted in the formation of a mixture of the d-isomer, l- isomer and the mesomer. We were interested in studying the nitration, primarily, of the mesomers, and they were therefore isolated from the mixtures by alcohol.

Nitration of the hydrocarbons to obtain dinitro compounds was by means of nitric acid in a medium of acetic anhydride, as we had found in nitrating meso-3,4-diphenylhexane that this gave much better yields than other methods of nitration.

Thus, the following p,p'-dinitro derivatives were synthesized: p,p'-dinitro-1,2-diphenylethane (II, R = H) [15,16], meso-p,p'-dinitro-2,3-diphenylbutane (II, $R = CH_3$) [17], meso-p,p'-dinitro-3,4-diphenylhexane (II, R = C_2H_5) [18], racemic p,p'-dinitro-3,4-diphenylhexane (II, $R = C_2H_5$) [18], meso-p,p'-dinitro-4,5-diphenyloctane (II, $R = C_3H_7$) and meso-p,p'-dinitro-5,6-diphenyldecane (II, $R = C_4H_9$).

The first four of these dinitro derivatives are described in the literature.

The position of the nitro radical in the molecules of meso-p,p'-dinitro-4,5-diphenyloctane (II, $R = C_3H_7$) and meso-p,p'-dinitro-5,6-diphenyldecane (II, $R = C_4H_9$) was determined by converting them into their known dihydroxy derivative homologs: meso-p,p'-dihydroxy-4,5-diphenyloctane (IV, $R = C_3H_7$) [1] and meso-p,p'-dihydroxy-5,6-diphenyldecane (IV, $R = C_4H_9$) [14].

Comparison of the yields of the dinitro derivatives obtained shows that the presence of two alkyls in the 1,2-positions greatly facilitates entry of the nitro radical into the p and p'-positions.

Thus, for example, the yield of p,p'-dinitro-1,2-diphenylethane (II, R = H) attained only 20% of the theoretical, while, when the meso-forms of the diphenylethane homologs were nitrated, the corresponding dinitro derivatives were obtained with considerably higher yields: meso-p,p'-dinitro-2,3-diphenylbutane (II, $R = CH_3$)   51%, meso-p,p'-dinitro-3,4-diphenylhexane (II, $R = C_2H_5$)   66%, meso-p,p'-dinitro-4,5-diphenyloctane (II, $R = C_3H_7$) 62.1%, and meso-p,p'-dinitro-5,6-diphenyldecane (II, $R = C_4H_9$)   64.5%.

Nitration of meso-3,4-diphenylhexane (V) with the nitrating mixture gave meso-o,o',p,p'-tetranitro-3,4-diphenylhexane (VI).

This substance had been obtained by Fodor and Wein [18], but they took it erroneously for a trinitro derivative.

We confirmed the composition of this tetranitro derivative by elementary analysis. By reduction, we obtained the homologous tetraamino derivative (VII), whose composition was also confirmed by analysis. We obtained this same tetranitro derivative by reacting the nitrating mixture with meso-p,p'-dinitro-3,4-diphenylhexane (II, $R = C_2H_5$). It is clear from the foregoing that this compound apparently is described by formula (VI).

We usually employed iron filings and a mixture of acetic and hydrochloric acids to reduce the dinitro derivatives. Thus we obtained p,p′-diamino-1,2-diphenylethane (III, R = H) [15], meso-p,p′-diamino-2,3-diphenylbutane (III, R = CH_3) [19], meso-p,p′-diamino-3-4-diphenylhexane (III, R = C_2H_5) [18,20], racemic p,p′-diamino-3,4-diphenylhexane (III, R = C_2H_5) [18,20], meso-p,p′-diamino-4,5-diphenyloctane (III, R = C_3H_7) and meso-p,p′-diamino-5,6-diphenyldecane (III, R = C_4H_9).

Isolation of racemic p,p′-diamino-3,4-diphenylhexane (III, R = C_2H_5) after reduction with iron filings proved difficult. We reduced racemic p,p′-dinitro-3,4-diphenylhexane with stannous chloride.

The literature contains two different melting points for racemic p,p′-diamino-3,4-diphenylhexane, i.e., 63-65° [20] and 80°[18]. We obtained this compound with an m.p. of 70-71°. This difference in melting point is apparently to be explained by an admixture of the meso-form in the racemate. We removed the meso-form contaminant from the racemate by use of the low solubility of the hydrochloride of this compound in hydrochloric acid.

The following p,p′-dihydroxy derivatives were obtained by diazotizing the p,p′-diamino-1,2-diphenylethane homologs in a hydrochloric acid solution, followed by decomposition of aqueous solutions of the diazo compounds by heat: meso-p,p′-dihydroxy-2,3-diphenylbutane (IV, R = CH_3) [1], meso-p,p′-dihydroxy-3,4-diphenylhexane (IV, R = C_2H_5) [1], meso-p,p′-dihydroxy-4,5-diphenyloctane (IV, R = C_3H_7) [1], and meso-p,p′-dihydroxy-5,6-diphenyldecane (IV, R = C_4H_9) [14]. These p,p′-dihydroxy derivatives have all been described previously, but only meso-p,p′-3,4-dihydroxy-diphenylhexane (IV, R = C_2H_5) had been obtained by diazotization of the diamino derivative homolog [18].

Our experiments showed that at the point at which the foregoing p,p′-dihydroxy derivatives are produced from the corresponding p,p′-diamino derivatives, the readiness with which the amino group is converted to the hydroxy group was dependent to a considerable degree upon the length of the carbon chains in the 1,2-positions; the best results were obtained with methyl and ethyl radicals (60 to 73%).

EXPERIMENTAL

Meso-2,3-diphenylbutane. 53.7 g (30 ml) 2,3-dibromobutane was added in 40 minutes, with stirring and cooling of the mixture by salt and ice, to 7.8 g aluminum trichloride and 88 ml distilled benzene, stirring being continued for another 4.5 hours.

The next day the contents of the reaction flask were poured into 200 ml water, carefully shaken, the aqueous layer extracted with 30 ml benzene, the benzene solution washed in 20 ml water and distilled. Upon distillation of the benzene and redistillation the following fractions were obtained: 1st to 145° / 26 mm, 6.7 g; 2nd 150-195° 27 mm, 16.7 g; residue 10.4 g.

42 ml ethyl alcohol was added to the second fraction, and the whole was heated until dissolved. On the following day the precipitate was filtered, washed with alcohol and dried at 50°. 4.8 g meso-2,3-diphenylbutane, m.p. 123-125° was obtained. Yield 9.1%, measured in terms of 2,3-dibromobutane.

Meso-3,4-diphenylhexane and racemic 3,4-diphenylhexane. 174 g 1-phenyl-1-chloropropane (b.p. 95-99° / 22 mm) in 75 ml ether was added in 50 minutes to 120 ml dry ether, 15.2 g magnesium filings, and 0.75 g iodine that had been heated together until the ether began to boil. The reaction usually began in 5 to 10 minutes after the first 10 ml of the chloride solution had been added, as could be seen from the appearance of a gray precipitate, and it continued with evolution of heat. The reaction was accompanied by vigorous boiling of the ether, which was controlled by the rate at which the chloride was added and by the amount of heating; heating was continued for 7 hours after the last of the chloride had been added. Then, under water cooling, the following were gradually added to the reaction mixture: 75 ml water followed by a solution of 75 ml concentrated hydrochloric acid and 75 ml water. The supernatant ether layer was washed with water, the ether and the low boiling fraction were distilled over a boiling water bath, toward the end in a 17 mm vacuum. 175 ml ethyl alcohol was added to the residue, which was then heated until dissolved, and the mixture was cooled with salt and ice over night.

The precipitate was filtered, washed with alcohol and dried at 40-50°. 12.5 g meso-3,4-diphenylhexane, m.p. 86.87°, was obtained.

The alcoholic mother liquor was distilled. 130 ml alcohol was added to the fraction collected between 162° / 19 mm and 192° / 15 mm, totalling 65 g, whereupon another 8.5 g meso-3,4-diphenylhexane, m.p. 88-89° was obtained in exactly the same manner as before. The total yield of meso-3,4-diphenylhexane was 21 g, constituting 15.5%, measured in terms of the chloride.

The alcoholic mother liquor was distilled at normal pressure with the purpose of isolating racemic 3,4-di-

phenylhexane. A 42 g fraction obtained between 286 and 300° was redistilled. 35 g racemic 3,4-diphenylhexane, b.p. 292-302°, was obtained in this manner. The yield of racemic 3,4-diphenylhexane was 26.1% in terms of chloride.

11.3 g magnesium filings, 70 ml dry ether and 0.5 g iodine were used to produce 3,4-diphenylhexane from an ether solution of the undistilled 1-phenyl-1-chloropropane obtained by saturation of 110 g ethylphenylcarbinol with hydrogen chloride. There was an 18% yield of 3,4-diphenylhexane, and a 26% yield of the racemic form, in terms of ethylphenylcarbinol.

Meso-4,5-diphenyloctane. This compound was obtained under the same conditions as meso-3,4-diphenylhexane. By reacting 8.5 g magnesium filings in the presence of 0.4 g iodine and 70 ml dry ether with 107 g 1-phenyl-1-chlorobutane (b.p. 115-118° / 15-18 mm) dissolved in 30 ml ether, a fraction consisting of 33 g, b.p. 172-200° / 16 mm was obtained after the usual processing and distillation (no portion of the meso-4,5-diphenyloctane was isolated prior to distillation). 11.3 g precipitate was obtained from the above fraction after addition of 33 ml ethyl alcohol. 6.9 g meso-4,5-diphenyloctane, m.p. 97-98° was obtained after recrystallization from 40 ml alcohol. The yield was 8.2% calculated in terms of 1-phenyl-1-chlorobutane.

Meso-5,6-diphenyldecane. This was obtained in the same manner as meso-4,5-diphenyloctane. By reacting 4.5 g magnesium filings in presence of 0.2 g iodine and 35 ml dry ether with 62 g 1-phenyl-1-chloropentane (b.p. 115-120° / 15-16 mm) dissolved in 10 ml ether, a 21 g fraction, b.p. 196-220° / 16 mm was obtained after the usual processing and distillation. 9.6 g precipitate was obtained from this fraction by means of 21 ml ethyl alcohol. After recrystallization from 40 ml alcohol, 5.6 g meso-5,6-diphenyldecane, m.p. 78-79° was obtained. The yield was 12.4%, measured in terms of 1-phenyl-1-chloropentane.

p,p'-Dinitro-1,2-diphenylethane. 14 ml nitric acid (d 1.39) was added in 1 hour 15 minutes, with stirring and cooling by water for a reaction mixture temperature of 15-25°, to 10 g 1,2-diphenylethane (m.p. 50-52°) and 120 ml acetic anhydride. Stirring continued another 4.5 hours.

The next day, 50 ml water was added in an hour, with stirring and cooling; the precipitate was isolated by filtering, washed in dilute acetic acid and dried at 80°. Weight 9.7 g. The precipitate was then boiled with 50 ml ethyl alcohol, filtered while hot, and the undissolved portion washed on the filter with hot alcohol. Weight 3.8 g. M.p. 171-176°. After cooling of the alcoholic mother liquor, 3 g precipitate, m.p. 60-70° was obtained, but it failed to yield p,p'-dinitro-1,2-diphenylethane even after repeated recrystallization.

After recrystallization of the 3.8 g precipitate (171-176°) from 115 ml benzene, 3 g p,p'-dinitro-1,2-diphenylethane was obtained, m.p. 179-181°. Yield was 20% in terms of 1,2-diphenylethane.

The p,p'-dinitro derivatives described below were obtained in the same manner.

Meso-p,p'-dinitro-2,3-diphenylbutane. To 7 g meso-2,3-diphenylbutane (m.p. 123-125°) and 77 ml acetic anhydride was added, as in the previous experiment, 10 ml nitric acid (d 1.39). 7 ml water was added to the reaction mixture on the following day. The precipitate obtained was filtered and dried at 120°. The weight of the precipitate was 6.6g. After recrystallizing the precipitate from 250 ml acetic acid there was obtained 5.1 g meso-p,p'-dinitro-2,3-diphenylbutane, m.p. 254-256°, white in color. Yield was 51%.

Found %: N 9.27, 9.34. $C_{16}H_{16}O_4N_2$. Calculated %: N 9.33.

Meso-p,p'-dinitro-3,4-diphenylhexane. 33 g meso-3,4-diphenylhexane (m.p. 86-87°) was nitrated in 330 ml acetic anhydride by 41 ml nitric acid (d 1.39). The next day 54 ml water was added, the precipitate was filtered, washed with acetic acid and dried at 100°. The precipitate weighed 34.1 g, m.p. 170-172°; yield 75%. After recrystallization from 285 ml acetic acid, 30 g meso-p,p'-dinitro-3,4-diphenylhexane was obtained, m.p. 171-173°, color white. Yield 66%.

Found %: C 65.74, 65.63; H 6.21, 6.10; N 8.42, 8.84. $C_{18}H_{20}O_4N_2$. Calculated %: C 65.85; H 6.10; N 8.54.

Meso-p,p'-dinitro-4,5-diphenyloctane. After nitration of 5.6 g meso-4,5-diphenyloctane (m.p. 97-98°) in 50 ml acetic anhydride by 6.2 ml nitric acid (d 1.39), and addition of 8.1 ml water to the reaction mixture, after 12 hours the precipitate was filtered, and it weighed, after washing in dilute acetic acid and drying at 80°, 5.6 g, m.p. 161-165°.

After recrystallization from 40 ml acetic acid, 4.65 g meso-p,p'-dinitro-4,5-diphenyloctane, white in color, m.p. 170-171.5°, was obtained. Yield 62.1%.

0.1514, 0.1400 g sub.: 0.3742, 0.3466 g CO_2; 0.0920, 0.0857 g H_2O. 0.3052, 0.2269 g sub.: 20.8 ml N_2 (19°, 734 mm); 15.5 ml N_2 (20°, 740 mm). Found %: C 67.41, 67.51; H 6.80, 6.85; N 7.70, 7.75. $C_{20}H_{24}O_4N_2$. Calculated %: C 67.42; H 6.74; N 7.87.

Meso-p,p'-dinitro-5,6-diphenyldecane. 8 g meso-5,6-diphenyldecane (m.p. 78-79°) was nitrated in 66 ml acetic anhydride by 8.2 ml nitric acid (d 1.39). The next day, 10.8 ml water was added, the precipitate filtered, washed with acetic acid and dried at 80°. The weight was 8.2 g, the m.p. 147-149°. After recrystallization from 50 ml acetic acid, 6.75 g meso-p,p'-dinitro-5,6-diphenyldecane was obtained, white in color and with an m.p. of 153-155°. Yield was 64.6%.

0.0961, 0.1964 g sub.: 0.2406, 0.4948 g CO_2; 0.0646, 0.1266 g H_2O. 0.3096, 0.2876 g sub.: 19.20 ml N_2 (20°, 762 mm); 18.3 ml N_2 (29°, 739.4 mm). Found %: C 68.32, 68.75; H 7.52, 7.21; N 7.20, 7.00. $C_{22}H_{28}O_4N_2$. Calculated %: C 68.75; H 7.29; N 7.29.

Racemic p,p'-dinitro-3,4-diphenylhexane. 40 g racemic 3,4-diphenylhexane (b.p. 292-302°) was nitrated in 400 ml acetic anhydride by 50 ml nitric acid (d 1.39). Next day, 650 ml water was added. The nitration product separated out as a viscous mass. After repeated washing by decanting with water, separation of the water layer and drying at 100°, 55.4 g impure racemic p,p'-dinitro-3,4-diphenylhexane (an oil), was obtained, out of which a small quantity of meso-p,p'-dinitro-3,4-diphenylhexane crystals precipitated after 15 days.

Meso-o,o',p,p'-tetranitro-3,4-diphenylhexane. 10 g meso-3,4-diphenylhexane (m.p. 86-87°) was added in 10 minutes, with stirring and cooling, to a nitrating mixture composed of 80 ml sulfuric acid (d 1.84) and 40 ml nitric acid (d 1.51). The whole was then stirred and heated for two hours over a water bath at a temperature of 46-48° in the reaction mixture; after cooling it was poured into a mixture of water and ice. The precipitate was filtered and dried at 60°. The weight was 17.2g. Recrystallization from 480 ml acetic acid gave 11.6 g meso-o,o',p,p'-tetranitro-3,4-diphenylhexane, m.p. 216-218° (corrected), white in color, with a pale yellow tint. Yield was 66%.

0.1505, 0.1724 g sub.: 0.2859, 0.3286 g CO_2; 0.0619, 0.0706 g H_2O. 0.1974, 0.1540 g sub.: 24.3 ml N_2 (21°, 731 mm); 18.5 ml N_2 (22°, 733 mm). Found %: C 51.80, 51.98; H 4.60, 4.58; N 13.75, 13.41. $C_{18}H_{18}O_8N_4$. Calculated %: C 51.67; H 4.31; N 13.40.

p,p'-Diamino-1,2-diphenylethane. 5.8 g p,p'-dinitro-1,2-diphenylethane (m.p. 179-181°) was dissolved with heating in 105 ml acetic acid, whereupon 17.4 g iron shavings and 105 ml hydrochloric acid (d 1.19) were added together, the first, however, within 30 minutes, and the second in 2.5 to 3 hours. The reaction was conducted with an air condenser, under constant heating to 100-110° of the reaction mixture. After dissolution of the iron filings the mixture of acetic and hydrochloric acids was distilled over a boiling water bath at a final pressure of 50-60 mm. 417 ml saturated sodium chloride solution was added to the dry residue, and the mixture was heated for half an hour over a boiling water bath to dissolve the iron chloride.

The next day, the residue of impure dihydrochloride of the diamino product was filtered off, washed repeatedly with a saturated sodium chloride solution, dissolved with heating in 400 ml water, the solution boiled 20 minutes with 1.5 g activated charcoal, filtered, and the hot filtrate poured into 15 ml concentrated ammonia solution, diluted with 40 ml water. After cooling the residue of impure diamino product was filtered off and recrystallized from 3500 ml water in the presence of 1 g activated charcoal. This gave 3.1 g p,p'-diamino-1,2-diphenylethane having a very faint violet tint, m.p. 137-139°. Yield was 68.6%. The meso-diamino derivatives described below were obtained in the same manner and purified out of dilute alcohol.

Meso-p,p'-diamino-2,3-diphenylbutane. 11.2 g meso-p,p'-dinitro-2,3-diphenylbutane (m.p. 254-256°) was dissolved with heating in 535 ml acetic acid and reduced by the addition of 30.3 g iron filings and 198 ml hydrochloric acid (d 1.19). The reaction mixture was heated for 8 hours until complete solution of the iron. After processing conducted as in the preceding experiment, an impure diamino product precipitate separated out, which was boiled in the presence of activated charcoal in 120 ml ethyl alcohol diluted with 20 ml water. The hot filtrate was dissolved in 200 ml hot water. Upon drying at 100°, this gave 6 g meso-p,p'-diamino-2,3-diphenylbutane, white in color, m.p. 170-172°. Yield was 67%.

Found %: N 11.50, 11.46; $C_{16}H_{20}N_2$. Calculated %: N 11.67.

Meso-p,p'-diamino-3,4-diphenylhexane. Reduction of 15 g meso-p,p'-dinitro-3,4-diphenylhexane (m.p. 171-172°) in 225 ml acetic acid solution was performed by addition of 36.7 g iron filings and 225 ml hydrochloric acid (d 1.19).

The impure diamino precipitate produced after processing was boiled in the presence of activated charcoal in

150 ml ethyl alcohol, dissolved in 30 ml water. The hot filtrate was dissolved in 300 ml water. After drying at 80°, this gave 10.1 g precipitated meso-p,p'-diamino-3,4-diphenylhexane, white in color, m.p. 140-142°. Yield 82.4%.

Found %: C 80.21, 80.12; H 8.71, 8.60. $C_{18}H_{24}N_2$. Calculated %: C 80.60; H 9.00.

Meso-p,p'-diamino-4-5,diphenyloctane. 3 g meso-p,p'-dinitro-4,5-diphenyloctane (m.p. 170-171.5°) dissolved in 42 ml acetic acid was reduced by the addition of 6.9 g iron filings and 42 ml hydrochloric acid (d 1.19). After distillation of the acid mixture and treatment of the dry residue with 190 ml saturated sodium chloride solution, the diamino dihydrochloride product precipitate separated out, and was then dissolved upon heating in 350 ml water. The solution was boiled with activated charcoal, filtered, and the hot filtrate poured into a dilute ammonia solution.

The impure diamino precipitate was boiled in the presence of activated charcoal in 30 ml ethyl alcohol, and the hot filtrate was diluted with 35 ml hot water. After drying at 80°, 2 g white precipitated meso-p,p'-diamino-4,5-diphenyloctane, m.p. 129-130°, was obtained. Yield 80%.

0.0888, 0.1924 g sub.: 0.2643, 0.5724 g CO_2; 0.0762, 0.1668 g H_2O. 0.1976, 0.2039 g sub.: 16.7 ml N_2 (23°, 742 mm); 16.45 ml N_2 (21.5°, 740 mm). Found %: C 81.22, 81.18; H 9.60, 9.70; N 9.51, 9.14. $C_{20}H_{28}N_2$. Calculated %: C 81.08; H 9.46; N 9.46.

Meso-p,p'-diamino-5,6-diphenyldecane. 4.3 g meso-p,p'-dinitro-5,6-diphenyldecane (m.p. 153-155°) dissolved in 56 ml acetic acid was reacted with 9.2 g iron filings and 56 ml hydrochloric acid (d 1.19), whereupon the usual processing produced an impure diamino product precipitate which was boiled in 30 ml ethyl alcohol diluted with 5 ml water, in the presence of activated charcoal. The hot filtrate was dissolved in 60 ml hot water. The diamino product, separated out in the form of oily drops, crystallized as it cooled. 2.87 g white meso-p,p'-diamino-5,6-diphenyldecane, m.p. 105-106.5° was obtained. Yield was 79.1%.

0.1720, 0.1141 g sub.: 0.5136, 0.3404 g CO_2; 0.1557, 0.1016 g H_2O. 0.2896, 0.2217 g sub.: 23.2 ml N_2 (24°, 732.2 mm); 18 ml N_2 (25.5°, 727.8 mm). Found %: C 81.49, 81.41; H 10.13, 9.96; N 8.87, 8.89. $C_{22}H_{32}N_2$. Calculated %: C 81.48; H 9.88; N 8.64.

Racemic p,p'-diamino-3,4-diphenylhexane. A solution of 36 g crystalline stannous chloride ($SnCl_2 \cdot 2H_2O$) in 38 ml hydrochloric acid (d 1.19), brought almost to be boiling point, was added in a few minutes to a solution, also almost boiling, of 7 g oily   racemic p,p'-dinitro-3,4-diphenylhexane in 60 ml glacial acetic acid. The reaction mass was then heated for two hours at 80°.

On the following day most of the acetic and hydrochloric acid mixture was distilled off in vacuum over a water bath. 50 ml glacial acetic acid was added to the residue, and the precipitate deposited was filtered off after standing for 9 hours. The precipitate was dissolved in 150 ml water, and the tin was precipitated by hydrogen sulfide. The filtrate was evaporated till dry, and the dry residue dissolved in 15 ml hydrochloric acid (d1.19). If, at this point, the meso derivative hydrochloride was precipitated, it was filtered off. The filtrate was diluted with 50 ml water, boiled with activated charcoal and, when cooled, poured into a dilute ammonia solution. The precipitate was filtered out on the following day. The weight of the air-dried precipitate was 1.5 g. M.p. 65-67°. The rose-tinted precipitate was dissolved in 30 ml ether, the solution boiled with activated charcoal, filtered free of the charcoal after cooling, and hydrogen chloride was passed through the filtrate; this resulted in separation of an oily hydrochloride. The ether was poured off, and the hydrochloride was dissolved in 30 ml water, shaken cold with activated charcoal, and the filtrate poured into a dilute ammonia solution. This resulted in clouding at first, followed by precipitation after 10 to 12 hours. 1.16 g white racemic p,p'-diamino-3,4-diphenylhexane, m.p. 70-71° was obtained. Yield 20.3%.

0.1610, 0.1227 g sub.: 0.4759, 0.3622 g CO_2; 0.1296, 0.1000 g H_2O. 0.1616, 0.1505 g sub.: 14.1 ml N_2 (20°, 764.6 mm); 13.65 ml N_2 (21°, 740 mm). Found %: C 80.62, 80.50; H 9.01, 9.12; N 10.20, 10.25. $C_{18}H_{24}N_2$. Calculated %: C 80.60; H 9.00; N 10.44.

Meso-o,o',p,p'-tetraamino-3,4-diphenylhexane. 70 g stannous chloride dissolved in 172 ml hydrochloric acid (d 1.19) and brought almost to the boiling point was poured, in several doses during a few minutes time, into 8.6 g meso-o,o',p,p'-tetranitro-3,4-diphenylhexane (m.p. 216-218° − corrected) dissolved in 400 ml glacial acetic acid, also almost boiling, in a 2000 ml flask. The solution was then heated with an air condenser for an hour at almost the boiling pontt. On the following day the precipitate was filtered out, washed in acetic acid, and dried at 50°. White in color, and weighing 18.5 g, the precipitate was dissolved in 250 ml water, the tin precipitated by hydrogen sulfide, the filtrate evaporated to dryness, the residue dissolved in 150 ml water, the solution shaken for 30 minutes with 0.4 g activated charcoal, filtered, and the filtrate poured into a cooled solution of 8 ml concentrated ammonia in 50 ml water. This gave 4.28 g air-dried precipitate, white in color, m.p. 241-243°. The precipitate was dissolved in a mixture of 42 ml ethyl alcohol, 42 ml water, 12 ml hydrochloric acid (d 1.19), shaken at room temperature with activated

charcoal and, the next day, after filtering, was poured, with cooling, into a solution of 85 ml alcohol and 27 ml concentrated ammonia. A crystalline deposit gradually began to precipitate. 3.7 g white meso-o,o'p,p'-tetraamino-3,4-diphenylhexane, m.p. 248-250° was obtained. Yield 60.3%.

0.1555, 0.1267 g sub.: 0.4130, 0.3360 g CO_2; 0.1202, 0.1000 g H_2O. 0.1262, 0.1148 g sub.: 20.8 ml N_2 (21°, 742.6 mm); 18.85 ml N_2 (24°, 763.5 mm). Found %: C 72.43, 72.32; H 8.65, 8.83; N 18.70, 18.95. $C_{18}H_{26}N_4$. Calculated %: C 72.48; H 8.72; N 18.79.

Meso-p,p'-dihydroxy-2,3-diphenylbutane. 2 g meso-p,p'-diamino-2,3-diphenylbutane (m.p. 170-172°) was dissolved in dilute hydrochloric acid (1400 ml water and 22 ml hydrochloric acid, d 1.15). and was diazotized with stirring at room temperature by a solution of 1.3 g sodium nitrite in 50 ml water. The whole was then stirred for an hour, the reaction flask placed in a water bath, heated to 75°, and the heating continued for another hour at a temperature of 90° in the flask. The precipitate was filtered off on the following day, then stirred at room temperature for several hours in a solution of 2 g potassium hydroxide in 135 ml water, the solution filtered free of a deposit that formed in negligible quantity, and the filtrate poured into dilute hydrochloric acid. The precipitate deposited was recrystallized in the presence of activated charcoal from 25 ml acetic acid diluted with 20 ml H_2O. 1.4 g white meso-p,p' dihydroxy-2,3-diphenylbutane,   m.p. 229-231°, was obtained. Yield 69.4%. The dihydroxy derivatives described below were obtained in the same manner.

Found %: C 78.97; H 7.10. $C_{16}H_{18}O_2$. Calculated %: C 79.34; H 7.44.

Meso-p,p'-dihydroxy-3,4-diphenylhexane. Diazotization of 5 g meso-p,p'-diamino-3,4-diphenylhexane (m.p. 140-142°), dissolved in 3500 ml water and 55 ml hydrochloric acid (d 1.15) was performed by means of 3.3 g sodium nitrite solution in 125 ml water.

Dissociation of the diazo solution and purification of the deposited precipitate by means of a dilute potassium hydroxide solution proceeded as in the prior experiment. The alkali filtrate was poured into dilute hydrochloric acid, and the precipitate thus formed was dissolved in 125 ml ethyl alcohol diluted with 100 ml water, boiled with 2 g activated charcoal, filtered, and the hot filtrate dissolved in 125 ml hot water. 3.7 g white meso-p,p'-dihydroxy-3,4-diphenylhexane   was obtained, m.p. 184-186°. Yield 73.4%.

A sample mixed with sinestrol obtained from anethol did not cause depression in m.p.

Found %: C 79.73; H 8.22. $C_{18}H_{22}O_2$. Calculated %: C 80.00; H 8.15.

Meso-p,p'-dihydroxy-4,5-diphenyloctane. 0.9 g meso-p,p'-diamino-4,5-diphenyloctane (m.p. 129-131°) was dissolved in 580 ml water and 4.6 ml hydrochloric acid, and diazotized by a solution of 0.5 g sodium nitrite in 25 ml water. The usual processing gave 0.4 g of a brownish impurity that did not dissolve in dilute potassium hydroxide solution. After neutralization, a precipitate was deposited by the alkaline filtrate. The weight of the precipitate, after drying at 80°, was 0.35 g, m.p. 164-165°. Yield 39%. After solution in 6 ml ethyl alcohol and dilution of the heated alcohol solution with 14 ml hot water 0.3 g white meso-p,p'-dihydroxy-4,5-diphenyloctane, m.p. 165-166° was obtained. Yield 33.1%.

Found %: C 80.38; H 9.04. $C_{20}H_{26}O_2$. Calculated %: C 80.54; H 8.72.

Meso-p,p'-dihydroxy-5,6-diphenyldecane. Diazotization of 1.2 g meso-p,p'-diamino-5,6-diphenyldecane (m.p. 105-106.5°), dissolved in 700 ml water and 5.5 ml hydrochloric acid, was performed by means of 0.6 g sodium nitrite solution in 25 ml water. The usual processing gave 0.8 g of a brown-colored admixture that would not dissolve in a dilute potassium hydrochloride solution. After neutralization, the alkali filtrate gave 0.17 g precipitate of yellow tint, m.p. 168-169°. Yield 14.1%. After dissolving this precipitate in 10 ml ethyl alcohol and dilution   of the heated filtrate in 10 ml hot water, 0.06 g meso-p,p'-dihydroxy-5,6-diphenyldecane was obtained, m.p. 170-170.5°. Yield 5%. Substitution of hydrochloric acid for diazotization by an equivalent quantity of sulfuric acid failed to improve yield.

Found %: C 80.62; H 9.24. $C_{22}H_{30}O_2$. Calculated %: C 80.98; H 9.20.

SUMMARY

1. A series of 1,2-diphenylethane, meso-2,3-diphenylbutane, meso and racemic 3,4-diphenylhexane, meso-4,5-diphenyloctane   and meso-5,6-diphenyldecane derivatives, containing nitro, amino and hydroxy groups at the p and p' positions, were obtained by a common procedure.

The properties of five compounds produced for the first time are described.

2. It was found that the presence of two alkyls in the 1-and 2-positions of diphenylethane facilitated entry of the nitro group into p and p' positions.

3. Substitution of the amino group by the hydroxy group through diazotization and subsequent decomposition, revealed that this substitution, always conducted under identical conditions, gave satisfactory yields (60-70%) when methyls or ethyls are in the 1 and 2 positions in the p,p'-diaminodiphenylethane molecule. When alkyls have an extended carbon chain, the yield is reduced: n-propyls 33-39%, n-butyls 5-14%.

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SYNTHESES BASED ON ANABASINE

VIII. SULFONATION OF ANABASINE WITH SULFURIC ACID

O. S. Otroschenko and A. S. Sadykov

In the preceding paper [1], sulfonation of anabasine with pyridine sulfotrioxide was described. In the present work results of a study of the sulfonation of anabasine (I) with sulfuric acid are given.

It has been possible to carry out the reaction under the conditions for the sulfonation of pyridine [2] , by heating a mixture of anabasine with a large excess of concentrated sulfuric acid, d 1.84 (4 moles of sulfuric acid per mole of anabasine) for a period of 15-18 hours at 290-300°. The sulfonic acid formed was isolated in the form of its barium salt. From it the sodium and potassium salts were obtained by exchange reactions. The sulfonic acid was obtained in free state by reacting an equimolecular amount of sulfuric acid with the barium salt. It was a crystalline compound which, upon heating to 350°, did not melt and did not decompose. Determination of the equivalent, and analysis of the barium, potassium, and sodium salts indicated that its molecular formula $C_{10}H_7N_2SO_3H$, corresponded to a,β-dipyridyl sulfonic acid.

The structure of the acid was proved by the following procedure. Upon fusing the potassium salt of a,β-dipyridyl-5-sulfonic acid with potassium cyanide, there resulted 5-nitril-a,β-dipyridyl in the form of a crystalline compound with m.p. 108-109°(V). The nitrile was characterized by preparation of the iodomethylate with m.p. 251-252°, and the picrate with m.p. 179-181°.

Proceeding from the oxidation reaction of 5-nitril-a,β-dipyridyl iodomethylate, which will be described below, it can be considered as established that addition of methyl iodide proceeds along the nitrogen of the β-substituted ring of pyridine (VIII). Upon heating with hydrochloric acid, the nitrile was saponified, forming a,β-dipyridyl-5-carboxylic acid — a crystalline compound with m.p. 281-283°, (VI). Upon decarboxylating this acid, [4], a,β-dipyridyl was obtained. This indicated that the sulfonic acid has a basic structure of a,β-dipyridyl (VII).

The position of the sulfonic acid group remained to be clarified. For this purpose, 5-hydroxy-a,β-dipyridyl was prepared from the sulfonic acid — a crystalline compound with m.p. 178-179°(III). Upon its oxidation with potassium permanganate in alkaline medium, nicotinic acid (IV) resulted. Its formation indicated that the a-substituted pyridine nucleus was ruptured, and that the hydroxy, and hence the nitrile, carboxyl and sulfonic groups are present in this ring. Position of these groups was determined by oxidation of the a,β-dipyridyl nitrile iodomethylate [5] (VIII). In this case a partial saponification of the nitrile group occurred. For complete saponification, the isolated acid was heated with concentrated hydrochloric acid, as the result of which pyridine dicarboxylic acid was obtained, in which one carboxyl group was formed at the expense of β-substituted pyridine ring oxidation, and the second at the expense of saponification of the nitrile group. The melting point, solubility in water, and some other qualitative reactions of the acid corresponded to isocinchomeronic acid. Identity was proved by determining the m.p. of a mixed sample with isocinchomeronic acid (IX). To obtain the isocinchomeronic acid, a-methyl-β' ethyl pyridine [ ] was synthesized, and oxidized by potassium permanganate. The physical constants of isocinchomeronic acid obtained from a-methyl-β'-ethylpyridine corresponded to the literature data [7]. Proceeding from this fact, the authors considered that the sulfonic acid, the nitrile, and the a,β-dipyridyl carboxylic acid are the 5-substituted derivatives of a,β-dipyridyl. The formation of a,β-dipyridyl-5-sulfonic acid indicated that upon sulfonating anabasine, dehydrogenation of the piperidine ring takes place, as in an analogous reaction with piperidine[3].

To confirm the structure of 5-hydroxy-a,β-dipyridyl, it was necessary to carry out an additional study, since cases are known in the literature where the hydroxy group enters another position upon alkaline fusion of the sulfonic acid.

The scheme for sulfonation of anabasine and chemical conversion of the 5-sulfonic acid of a,β-dipyridyl is as follows.

H₂SO₄ 300° ... SO₃H (II) ... KOH ... OH (III) ... KMnO₄(OH') ... COOH (IV)

KCN ... CN (V) ... HOH (H') ... COOH (VI) − CO₂ ... (VII)

CH₃I ... CN N−CH₃ I (VIII) ... Ag₂O ... CN N−OH CH₃ ⇅ CN =O N−CH₃ ... KMnO₄ ... COOH HOOC N (IX)
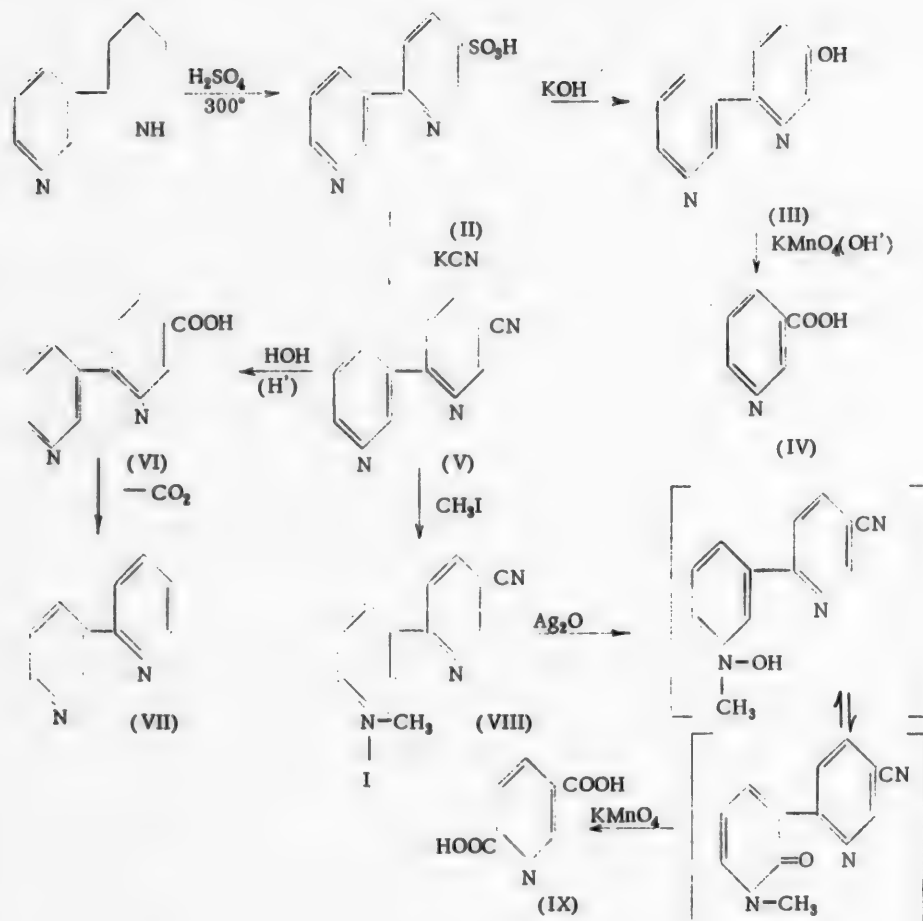
EXPERIMENTAL

Sulfonation of Anabasine with Sulfuric Acid.

112 ml of sulfuric acid (d = 1.84) was added to 84 g of anabasine, purified via the hydrochloride, in small portions with cooling. The resulting mixture was heated on a sand bath for 15 hours. At 270-280°, the mixture frothed considerably, after which uniform boiling proceeded. The mixture was heated at 300° for 2 to 3 hours. After cooling, the reaction mixture was boiled with barium carbonate suspension for 30 minutes (to a neutral or weakly alkaline reaction toward litmus). The solution was filtered. The filtrate, after separation of the barium sulfate and carbonate mixture, was boiled with carbon and evaporated to a small volume on a water bath. After cooling, there precipitated from the solution a crystalline precipitate which was filtered and washed with alcohol. There resulted 50.6 g of the barium salt of 5-sulfonic acid of α,β-dipyridyl (yield 31.4 %). The mother liquor was evaporated and distilled at 174-178° (5-6 mm); an oil resulted in this case (picrate of the oil had a m.p. of 154-156°). A sample mixed with α,β-dipyridyl picrate had a m.p. of 160-162°.

The barium salt, recrystallized from water with added carbon, was in the form of a white cyrstalline product, with mother-of-pearl shade, insoluble in alcohol. The salt was dried in vacuo (1-2 mm) at 100°.

0.06348 g sub.: 0.02509 g $BaSO_4$. 0.12288 g sub.: 0.04779 g $BaSO_4$. Found %: Ba 22.33, 22.89. $C_{10}H_7N_2SO_3 \cdot \frac{1}{2}$ Ba. Calculated %: Ba 22.65.

α,β-Dipyridyl-5-sulfonic acid Potassium Salt. Prepared by adding an equimolecular amount of potassium carbonate to a solution of the barium salt; the filtrate, after separation of the barium carbonate, was evaporated. Alcohol was added to the solution. A precipitate crystallized upon standing, which was then recrystallized from water with

added alcohol. The potassium salt was soluble in water, insoluble in alcohol.

0.10845 g sub.: 0.03439 g K_2SO_4. 0.10828 g sub.: 0.03499 g K_2SO_4. Found %: K 14.17, 14.44. $C_{10}H_7N_2SO_3K$. Calculated %: K 14.18.

Sodium Salt of a,β-Dipyridyl-5-sulfonic Acid. Prepared in a manner analogous to that for the potassium salt. After separation of the $BaCO_3$ precipitate, the filtrate was evaporated to dryness. The salt was recrystallized from alcohol. The sodium salt was readily soluble in water, poorly so in alcohol, and when air-dried, contained 1 molecule of water of crystallization.

0.060441 g sub.: 0.014716 g Na_2SO_4. 0.071014 g sub.: 0.017623 g Na_2SO_4. Found %: Na 7.89, 7.05. $C_{10}H_7N_2SO_3Na \cdot H_2O$. Calculated %: Na 7.80.

Determination of the water of crystallization was carried out by drying in vacuo at 2 mm and 150°.

0.2572 g sub.: 0.0299 g H_2O. $C_{10}H_7N_2SO_3Na \cdot H_2O$. Calculated: : 0.0314 g H_2O.

a,β-Dipyridyl-5-sulfonic Acid

The calculated amount of sulfuric acid was added to a solution of 10 g of the barium salt of a,β-dipyridyl-5-sulfonic acid. After removal of $BaSO_4$, the precipitate was evaporated on a water bath to small volume. The a,β-dipyridyl-5-sulfonic acid crystallized out from the solution upon standing, in the form of mother-of-pearl platelets. The acid was poorly soluble in water, insoluble in alcohol; it was recrystallized from water. For analysis, the acid was dried in vacuo (1 mm) at 100°.

0.0694, 0.0792 g sub.: 3.50, 3.40 ml 0.09901 N NaOH. Found: Equiv. 234.0, 235.3. $C_{10}H_7N_2SO_3H$. Calculated: Equiv. 237.0.

3.778, 3.422 mg sub.: 0.388 ml N_2 (16°, 731 mm); 0.378 ml N_2 (25°, 722 mm). Found %: N 11.11, 11.50. $C_{10}H_7N_2SO_3H$ Calculated %: N 11.81.

a,β-Dipyridyl-5-nitrile. 10 g of a,β-dipyridyl-5-sulfonic acid in potassium salt form was mixed thoroughly with 32 g of potassium cyanide; the mixture placed in a retort, was heated to 351°, whereupon the oil distilled off, crystallizing rapidly in the tube of the retort. Yield was 2.1 g (32.5%). The a,β-dipyridyl-5-nitrile was soluble in methyl alcohol, poorly so in ethyl alcohol and water, soluble in toluene with heat as well as in petroleum ether and benzene. The m. p. was 107-109° (from methyl alcohol, petroleum ether and toluene).

2.090, 3.012 mg sub.: 0.460, 0.625 ml N_2 (25°, 724 mm). Found %: N 23.01, 22.63. $C_{10}H_7N_2CN$. Calc. %: N 23.20.

The picrate was obtained by decanting off alcoholic solutions of a,β-dipyridyl-5-nitrile with picric acid. M. p. 180-182° (from alcohol).

2.255, 2.450 mg sub.: 0.415, 0.240 ml N_2 (24°, 724.5 mm). Found %: N 19.32, 19.73. $C_{10}H_7N_2CN \cdot C_6H_2(NO_2)_3OH$. Calculated %: N 20.44.

The Iodomethylate. 2 g of methyl iodide was added to a solution of 1 g of a,β-dipyridyl-5-nitrile. The precipitate crystallized from solution on the second day. There resulted 1.1 g of a,β-dipyridyl-5-nitrile iodomethylate. M. p. 243-245° (from water or methyl alcohol).

0.0314 g sub.: 0.0980 ml 0.1 N $AgNO_3$ (potentiometric titration). Found %: I 39.50. $C_{10}H_7N_2CN \cdot CH_3I$. Calc. %: I 39.10.

a,β-Dipyridyl-5-carboxylic Acid. 3 g of a,β-dipyridyl-5-nitrile was heated with concentrated hydrochloric acid for 6 hours. The solution was then evaporated to dryness. The residue was a,β-dipyridyl-5-carboxylic acid. 2.8 g (28.11%) of the acid was obtained.

a,β-Dipyridyl-5-carboxylic acid was very poorly soluble in water. It sublimed. M. p. 281-283°(from alcohol).

2.836, 2.871 mg sub.: 0.353 ml N_2 (20°, 729 mm); 0.362 ml N_2 (22°, 729 mm). Found %: N 13.92, 13.99. $C_{10}H_7N_2COOH$. Calculated %: N 14.0.

20.02, 21.09 mg sub.: 1.02, 1.01 ml 0.099 N NaOH. Found: Equiv. 198, 210. $C_{10}H_7N_2COOH$. Calc.: Equiv. 200.

a,β-Dipyridyl. 0.1 g of a,β-dipyridyl-5-carboxylic acid and 0.2 g of copper bronze were heated with 2 ml of benzene in a sealed tube at 210-230° for 4 hours. After breaking the seal, the solution was filtered. The residue, after distilling off the benzene, gave with picric acid in alcoholic solution a picrate melting at 164-165°. A sample mixed with a,β-dipyridyl picrate, obtained by dehydrogenation of anabasine, melted at 164-169°.

5-Hydroxy-a,β-dipyridyl. 9 g of potassium hydroxide was heated on a sand bath in a porcelain cup with 3 ml of water. 3 g of a,β-dipyridyl-5-sulfonic acid in the sodium salt form was added at a temperature of 190-200°. The mixture was stirred continuously. With increased temperature the melt solidified, and then liquified upon heating to 300°. Heating was continued for another 30 minutes, the melt then dissolved in a small volume of water, neutralized with hydrochloric acid, and extracted with ether. The ether extractions were dried. The ether was distilled off. The solid precipitate had a m. p. of 177-179° (from methyl alcohol). 5-Hydroxy-a,β-dipyridyl was poorly soluble in water and alcohol. It was readily soluble in acetone.

2.742 mg sub.: 0.392 ml N_2 (22°, 732 mm). 2.407 mg sub.: 0.482 ml N_2 (23°, 728 mm). Found %: N 15.97, 16.14. $C_{10}H_7N_2OH$. Calculated %: N 16.28.

The picrate was prepared by decanting off the alcoholic solution of 5-hydroxy-a ,β -dipyridyl with picric acid. M.p. was 217-219° (from water).

Nicotinic Acid.

An excess of saturated potassium permanganate solution was added to 3 g of 5-hydroxy-a ,β -dipyridyl in 20 % sodium hydroxide solution. Manganese dioxide was removed from the solution by filtration. The filtrate was evaporated to small volume and neutralized with hydrochloric acid. The acid was isolated in the form of its copper salt by adding to a neutral solution of copper acetate. The copper salt was decomposed with hydrogen sulfide. The acid, m p. 221-222°, was prepared successfully from the resulting precipitate (identified as nicotinic acid). Upon decarboxylation, pyridine resulted. The picrate of pyridine had a m.p. of 164-165°.

3,6-Pyridinedicarboxylic Acid.

2.2 g of the iodomethylate of 5-nitrile-a ,β -dipyridyl was dissolved with heating in 20 ml of water, and freshly-precipitated silver oxide (from 2 g of silver nitrate) added to the solution. The silver iodide precipitate was filtered off rapidly, and to the filtrate potassium permanganate gradually added. On the following day, the excess potassium permanganate was removed by addition of alcohol. After removal of manganese dioxide, the filtrate was evaporated to small volume and neutralized with concentrated hydrochloric acid. 0.2 g of the acid resulted. For complete saponification of the nitrile group, the acid was boiled with concentrated hydrochloric acid for 4 hours; the solution was then evaporated to dryness and the residue recrystallized from hot water. The acid dried at 100° (1 mm) had a m.p. of 252-253°.

SUMMARY

1. The sulfonation reaction of anabasine with sulfuric acid at 280-300° has been studied. It has been established that there takes place dehydrogenation of the piperidine ring of anabasine, forming a .β -dipyridyl-5-sulfonic acid.

2. The sodium, potassium and barium salts of a ,β -dipyridyl-5-sulfonic acid have been prepared.

3. Starting with a ,β -dipyridyl-5-sulfonic acid, there have been prepared: a ,β -dipyridyl-5-nitrile, characterized as the picrate and the iodomethylate, and a ,β -dipyridyl-5-carboxylic acid and 5-hydroxy-a ,β -dipyridyl, characterized as the picrates.

4. It has been established that the methyl iodide is located on the nitrogen of the β -substituted pyridine ring in a ,β -dipyridyl-5-nitrile.

5. The compounds which have been prepared are new and not described in the literature.

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• See Consultants Bureau English translation, page 917.

COMPOUNDS OF NICOTINE WITH CUPRIC CHLORIDE
AND CUPRIC BROMIDE

S. F. Babak and G. B. Kagramanova

In a preceding article [1], the synthesis of, and certain properties of, nicotine compounds with mercury chloride and bromide were described. The preparation and properties of compounds between cupric chloride and bromide and nicotine are described in the present work.

Amiel [2] upon dissolving nicotine hydrochloride in an aqueous solution of cupric chloride, and subsequently evaporating this solution, obtained bright-yellow crystals of the composition $[CuCl_4](C_{10}H_{14}N_2H_2) \cdot H_2O$. On dehydrating this compound, a dark-yellow compound of the composition $[CuCl_4](C_{10}H_{14}N_2H_2)$ was formed. The interaction of nicotine hydrobromide with cupric bromide in aqueous solution by the same authors produced lustrous black crystals of composition $[CuBr_4](C_{10}H_{14}N_2H_2)$.

The present authors have studied the interaction of cupric chloride with nicotine in acetone, and of cupric bromide with nicotine in ethyl alcohol.

EXPERIMENTAL

Commercial acetone and ethyl alcohol were doubly distilled. The nicotine, prepared from technical nicotine sulfate, boiled at 111-112° (6 mm), d_{25} 1.0068, η_{25} 3.8942. The cupric chloride and bromide used were chemically pure. The hydrochloric acid was purified by distillation.

$(CuCl_2)_2 \cdot C_{10}H_{14}N_2$. The compound was obtained as an amorphous yellow precipitate upon mixing acetone solutions in stoichiometric ratio of cupric chloride and nicotine (slight excess). The precipitate darkened in the presences of a trace of acetone and moisture of the air, and was therefore transferred quickly to a Schott filter covered with a stopper and calcium chloride tube and dropping funnel, washed several times with acetone and dried in a vacuum desiccator. The compound was in the form of a yellow powder, stable in air in the dry state. The yield of pure product was about 96% (melting with decomposition at 130-131°). Nitrogen was determined according to Dumas, nicotine determined by titration with sulfuric acid in the presence of methyl red, and after distilling twice from alkaline solution with steam, the halide was determined volumetrically according to Volhard, copper being determined iodometrically.

0.1352 g sub.: 0.1760 g AgCl. 0.1368 g sub.: 0.1752 g AgCl. 0.0174 g sub.: 0.0051 g Cu. 0.0202 g sub.: 0.0058 g Cu. 0.0986 g sub.: 6 ml N_2 (19°, 703 mm). 0.1428 g sub.: 8.6 ml N_2 (19°, 703 mm). Found %: Cl 32.15, 32.36: Cu 28.98, 29.05; N 6.57, 6.51. $(CuCl_2)_2C_{10}H_{14}N_2$. Calculated %: Cl 32.98; Cu 29.49; N 6.44.

The compound was readily soluble in water and dilute acids, very poorly soluble in chloroform and carbon tetrachloride, and insoluble in acetone, ethyl ether, ethyl alcohol, toluene and benzene.

$CuCl_2 \cdot C_{10}H_{14}N_2$. For preparation of this compound, cupric chloride and nicotine were taken in equimolecular amounts. As the nicotine was added to an acetone solution of cupric chloride, a beige-colored precipitate separated, changing to a green color, and finally fine, lustrous, brown crystals resulted, which were filtered, washed several times with acetone, and dried in a vacuum desiccator. The dry crystals were stable in air. Yield was 80%. Melting with decomposition at 120-121°.

0.1562 g sub.: 0.1514 g AgCl. 0.1499 g sub.: 0.1446 g AgCl. 0.0426 g sub.: 0.0092 g Cu. 0.0410 g sub.: 0.0090 g Cu. 0.1620 g sub.: 15.6 ml N_2 (29°, 700 mm). 0.1760 g sub.: 17 ml N_2 (30°, 700 mm). Found %: Cl 23.94, 23.82; Cu 21.54, 21.58; N 9.14, 9.42. $CuCl_2 \cdot C_{10}H_{14}N_2$. Calculated %: Cl 23.91; Cu 21.42; N 9.10.

The compound was insoluble in cold water, hydrolyzing in warm and hot water as with the preceding compound. Solubility was good in aqueous acid solution, but poor in chloroform and benzene. Solubility in benzene increased noticeably with increased temperature. Insoluble in acetone, ethyl ether, ethyl alcohol and toluene.

$2CuCl_2 \cdot 4C_{10}H_{14}N_2 \cdot 4HCl \cdot H_2O$. Dry hydrogen chloride was passed into a solution consisting of 1 g of cupric chloride and 40 ml of acetone until the dirty green color changed completely to red-brown, considerable spontaneous heat evolution being observed. After cooling the solution to room temperature, there was added dropwise 4 g of nico-

tine dissolved in acetone, with stirring. A milky-white solution and an oily liquid, dark-blue in color on the bottom of the flask, were formed. The oily liquid was separated and dissolved in a small amount of water. The resulting solution acquired a blue-green color. The solution was placed in a crystallizer, and after several days at room temperature, fine, blue, lustrous crystals were formed. The crystals were extracted, dried between sheets of filter paper, and then in a desiccator over calcium chloride. The yield was about 85%. The resulting compound was recrystallized from water. It melted with decomposition at 136°.

0.0938 g sub.: 0.1028 g AgCl. 0.1572 g sub.: 0.1798 g AgCl. 0.0452 g sub.: 0.0052 g Cu. 0.0264 g sub.: 0.0029 g Cu. 0.1578 g sub.: 16.2 ml N_2 (29°, 698 mm). 0.1061 g sub.: 9.8 ml N_2(18°, 703 mm). 0.3296 g sub.: 0.0050 g H_2O. 0.3602 g sub.: 0.0056 g H_2O. Found %: Cl 27.06, 27.30; Cu 11.34, 11.22; N 10.46, 10.26; H_2O 1.51, 1.51. $2CuCl_2 \cdot 4C_{10}H_{14}N_4 \cdot 4HCl \cdot H_2O$. Calculated %: Cl 26.27; Cu 11.75; N 10.26; H_2O 1.66.

Water determination was carried out by loss in weight of water on a portion of the compound, by heating to constant weight at 92°, whereupon the blue crystals became green. If left standing in air, however, they again acquired a blue color. The compound was readily soluble in water, forming a blue solution of acid reaction. It dissolved in ethyl alcohol but not in carbon tetrachloride, benzene, ethyl ether or acetone.

$CuCl_2 \cdot C_{10}H_{14}N_2 \cdot 2HCl$. This compound was prepared by Amiel by dehydrating the compound $[CuCl_4]$- -$(C_{10}H_{14}N_2H_2) \cdot H_2O$ at 80°. It was synthesized by the authors from the anhydrous compounds in dry acetone medium. For this purpose, cupric chloride and nicotine were taken in equimolecular amounts. The acetone solution of cupric chloride was saturated with hydrogen chloride, whereupon considerable spontaneous heat evolution was observed. In order to prevent air moisture from getting into the solution, suitable precautionary steps were taken. After the solution was at room temperature, an acetone solution of nicotine was added to it dropwise, whereupon a bright-yellow, powdery precipitate separated. The precipitate was separated from the solution, washed several times with acetone and dried in a vacuum desiccator. Yield of the compound obtained was about 78%. It melted with decomposition at 140-143°.

0.1770 g sub.: 0.2772 g AgCl. 0.1486 g sub.: 0.2318 g AgCl. 0.0252 g sub.: 0.0046 g Cu. 0.0248 g sub.: 0.0045 g Cu. 0.1782 g sub.: 13.6 ml N_2 (29°, 700 mm). 0.1644 g sub.: 13 ml N_2 (30°, 698 mm). Found %: Cl 38.68, 38.53; N 7.79, 8.04; Cu 17.86, 18.04. $CuCl_2 \cdot C_{10}H_{14}N_2 \cdot 2HCl$. Claculated %: Cl 38.42; N 7.57; Cu 17.9.

The compound was readily soluble in water, the solution having a strong acid reaction. Solubility in acetone and ethyl alcohol was low. Insoluble in chloroform, ethyl ether, toluene and benzene.

The authors also repeated synthesis of the compound $CuCl_2 \cdot C_{10}H_{14}N_2 \cdot 2HCl \cdot H_2O$, prepared by Amiel, and some of its properties which Amiel did not indicate in his work were determined. The compound resulted by interaction of equimolecular amounts of cupric chloride and nicotine in aqueous, strong hydrochloric acid medium, with subsequent crystallization of the product. Yield was 77%. It melted with decomposition at 129-130°. Orange-yellow crystals, readily soluble in water, with strongly acid reaction. The compound was readily soluble in 96% ethyl alcohol. Insoluble in carbon tetrachloride, benzene, toluene, ethyl ether and acetone.

$CuBr_2 \cdot C_{10}H_{14}N_2$. 4.8 g of nicotine, dissolved in alcohol, was added dropwise, with stirring, to a solution of 2.23 g cupric bromide and 50 ml of ethyl alcohol. Fine brown crystals separated and a blue-green solution resulted. The crystals were filtered off, washed with alcohol, and dried in a vacuum desiccator. The dry crystals were stable in air. Yield was about 77.7%. M.p. was 124.5-125°.

0.1782 g sub.: 13 ml N_2 (32°, 693.9 mm). 0.1778 g sub.: 13 ml N_2 (32°, 693.9 mm). 0.1508 g sub.: 0.0249 g Cu. 0.1482 g sub.: 0.0244 g Cu. 0.1500 g sub.: 0.0635 g Br_2. 0.1442 g sub.: 0.0603 g Br_2. 0.1482 g sub.: 0.0606 g Br_2. Found %: N 7.36, 7.37; Cu 16.55, 16.45; Br 41.10, 41.81, 40.84. $CuBr_2 \cdot C_{10}H_{14}N_2$. Calculated %: N 7.26; Cu 16.49; Br 41.46.

The compound was soluble in acids, hydrolyzing with water. It was poorly soluble in ethyl alcohol and benzene. It did not dissolve in carbon tetrachloride or ethyl ether. After separation of the compound $CuBr_2 \cdot C_{10}H_{14}N_2$, it was placed in a crystallizer, from which, after several days at room temperature, were formed silky-white, needle crystals. The crystals were separated from the mother liquor (blue-green in color), washed with ether, and air-dried. Yield was small, all told about 10%. M. P. was 137-140°. Repeated analysis of this compound indicated a composition of about 29.32% Br, 10.63% N, carbon and hydrogen present, but no copper. The compound dissolved in ethyl alcohol and acids, but was insoluble in carbon tetrachloride, ether and benzene.

Upon mixing alcoholic solutions of copper bromide and nicotine in the ratio of 1 : 1, the compound $CuBr_2 \cdot C_{10}H_{14}N_2$ immediately separated from solution. This compound was filtered, and from the filtrate after a period of time were formed fine, dark-red, crystals. The crystals were separated from the mother liquor, washed with alco-

hol, and dried. They were stable in air. Yield was negligible. M.p. was 245-246°. The compound was poorly soluble in alcohol and water. Solubility in nitric acid was good. Solubility was also good in a concentrated solution of sodium hydroxide, and a transparent, slightly-yellow solution was formed. Analysis indicated the presence of about 50% bromine, a high content of nitrogen, carbon and hydrogen being found, no copper being found in the compound. The last two compounds, not containing copper, whose quantitative composition have not yet been completely established, brings to mind the fact that copper bromide can brominate nicotine.

In studying the combination of nicotine with copper bromide and chloride, the latter's high reactivity should be mentioned. Depending upon conditions of the reaction course, they form several compounds with nicotine. There is the possibility of forming, under other conditions and solvents, compounds of copper bromide and chloride with nicotine of other compositions.

SUMMARY

1. A powdery compound of nicotine with copper chloride, of the composition $(CuCl_2)_2 \cdot C_{10}H_{14}N_2$, has been prepared.

2. Crystalline compounds of nicotine with copper chloride, of the composition $CuCl_2 \cdot C_{10}H_{14}N_2$; $2CuCl_2 \cdot 4C_{10}H_{14}N_2 \cdot 4HCl \cdot H_2O$, have been prepared.

3. A powdery compound of nicotine with copper chloride, of the composition $CuCl_2 \cdot C_{10}H_{14}N_2 \cdot 2HCl$, has been prepared (by a method differing from that known in the literature).

4. A crystalline compound of nicotine with copper bromide, of the composition $CuBr_2 \cdot C_{10}H_{14}N_2$, has been prepared.

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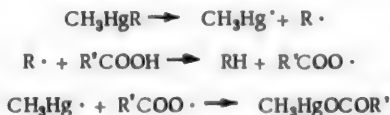[2] J. Amiel, Comptes rend., 200, 138 (1935); 201, 1383 (1935); Chem. Zentr., 1937, I, 314.

DISCUSSION

COMMENT ON THE ARTICLE BY A.A. BOLSHAKOVA:

INTERACTION OF METHYL-α -NAPHTHYLMERCURY AND METHYLPHENYLMERCURY WITH ORGANIC ACIDS

G. A. Razuvaev

In an article published recently by A. A. Bolshakova [1], the reactions of methyl-α -naphthylmercury and methylphenylmercury with a number of organic acids were described, which take place when the component is heated up to 75°. The reaction mechanism was presented by the following scheme:

$$CH_3HgR \rightarrow CH_3Hg^{\cdot} + R \cdot$$

$$R \cdot + R'COOH \rightarrow RH + R'COO \cdot$$

$$CH_3Hg \cdot + R'COO \cdot \rightarrow CH_3HgOCOR'$$

Such an interpretation of the reaction mechanism appears to the commentor as entirely unsubstantiated, and very unlikely. Decomposition of metallo-organic compounds of mercury into radicals proceeds at temperature much above that of 75°.. Furthermore, the R radical should have removed the hydrogen atoms from the α -carbon atoms of the chain, and to a lesser extent, from the carboxyl [2]. Finally, were the R'COO radical to appear, it would have to have a sufficient half-life period, without decomposing, in order to encounter the CH_3Hg radical. In the meantime, it is to be expected that the R'COO radicals, which are now known in some detail, would decompose at 75° into R' and CO_2. Thus, for example, during reaction of acetyl peroxide or of benzoyl with mercury, the CH_3COO- and C_6H_5COO-radicals decompose completely into CO_2 and methyl- or phenyl-radicals at 80° [3].

At present, there is grave doubt that the free radical mechanism of reaction proceeds with formation of a CH_3COO- radical without the evolution of CO_2; for example, the oxidation reaction of β -glycols with lead tetraacetate [4], or certain reactions of the nitrosoacylarylamines [5]. However, the decomposition of lead tetraacetate in acetic acid to form CH_3COO- radicals, proceeds with evolution of CO_2 and methane [6]. It is not understood why the author considers the methyl radical to be less reactive than the naphthyl or phenyl radicals. On the contrary, it is known that the most reactive is the non-stabilized methyl radical.

It should be considered that the interaction of metallo-organic compounds of mercury with acids proceeds along the line of an ionic mechanism, similar to their reaction with hydrogen chloride; it is therefore natural to expect complete coincidence in sequence of radical rupture by the Kharasch order, as was indicated in the aforementioned work.

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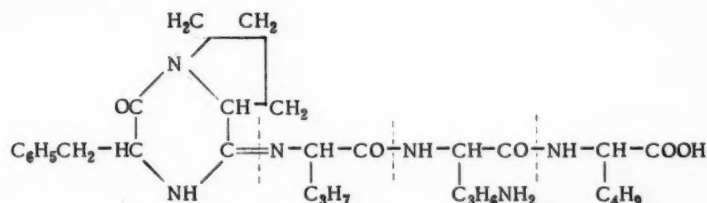
REGARDING THE STRUCTURE OF GRAMICIDIN C

M. S. Reznichenko

A recently-published paper by P. G. Ioanisiani, N. I. Gavrilova and M. O. Plekhan, " The Structure of Grami-cidin C" [1] advances an arbitrary modification of the well-demonstrated formula of gramicidin C (p.371)∗ . According to the assertion of these authors, the structure is characterized by the presence of a diketopiperazine heterocycle and a free saturated carboxyl group

$$H_2C \quad CH_2$$
$$C_6H_5CH_2-HC \quad OC \quad N \quad CH-CH_2 \quad C=N-CH-CO-NH-CH-CO-NH-CH-COOH$$
$$NH \quad C_3H_7 \quad C_3H_6NH_2 \quad C_4H_9$$

which is, however, not substantiated by any of the experimental data in the given work. Careful study of the material in this paper makes clear that the structure of gramicidin C advanced by the authors does not follow from the data they adduce, as is evident from the following.

1. The data of the paper in question completely lack any analytical evidence to support the presence in native or regenerated gramicidin of piperazine (or its derivatives) or of any quantity whatever of free carboxyl groups, which is in basic contradiction to the open structure the authors ascribe to gramicidin, which in reality is a cyclic polypep-tide compound [2].

2. Table 1 (p.373) of the work in question adduces data testifying to a sharp increase in the quantity of amine nitrogen in the regenerated gramicidin preparation, attaining 130 to 350% of its original content. This in-crease in amine nitrogen does not stand (and cannot stand) in any causal relationship, as the authors believe (p. 374)∗ to the presence of heterocyclic groups in the structure ascribed to gramicidin. The fact of increase in amine ni-trogen content, titrated by the Sörensen method or determined by the Van Slyke gasometric method, only demon-strates that gramicidin subjected to the conditions of experiment for a long period of time (more than 7 hours) in a mixture of concentrated hydrochloric and acetic acids (p.372)∗ underwent hydrolysis (at the broken line on the adduc-ed formula).

3. According to current biochemical concepts, the degree of hydrolysis of albuminous susbtances is practically controlled precisely by the quantity of increasing amine nitrogen. This being the case, the conclusion by Ioanisiani, Gavrilov and Plekhan that they had "demonstrated the presence in gramicidin C of two fragments of diketopiperazine and tripeptide" (p. 375)∗ on the basis of the observed rise in amine nitrogen, remains unsupported.

4. The method employed by these authors of electrical regeneration of peptides (and albumins) dissolved for this purpose in a mixture of concentrated hydrochloric and acetic acids, is defective. Aside from the fact that so powerful a reagent is itself capable, in several hours time, of causing hydrolysis of the peptide substance under study, its action causes, in reality, an even more profound change in the chemical nature of gramicidin. This conclusion is obvious upon examination of the data advanced on p. 373∗ where the authors note that after the electrical regenera-tion of gramicidin, it was impossible to find in its hydrolysis products two (of the total number of five) of its proved decomposition products: phenylaniline and proline.

5. The use of the method of research employed by the authors for the study of gramicidin cannot serve as an objective criterion for determining the nature of its internal structure, as it undergoes profound destructive changes under the given conditions of experiment. The diketopiperazine-amidine structure ascribed to gramicidin by Ioanis-iani, Gavrilov and Plekhan, being completely unsubstantiated, must be taken as fictitious and not reflecting the true nature of gramicidin C.

∗ The indicated pagination is that of the C.B. Translation.

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